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STANDARD ABSORPTION CURVES FOR SPECIFYING THE QUALITY OF X-RADIATION [1]

By Lauriston S. Taylor and George Singer

ABSTRACT

In the measurement of X-rays there is a proportionality between the energy in the beam and its strength in roentgens, only for radiation of the same effective spectral distribution. In previous work comparison with the copper and aluminum absorption curves produced by constant potential has been established as a means of equating the qualities of X-ray beams excited by various voltage wave forms. Therefore a set of standard absorption curves is set up for copper up to 180 kv (constant) and aluminum up to 110 kv (constant). Accurate evaluation of the wall absorption of the tubes used permits the establishment of basic absorption curves. Similar curves are given for potentials from 250 to 550 kv (constant) using a tube having 6 mm of copper filtration. The effect of wall absorption on the relative position of the absorption curves is discussed, and it is shown how for any given excitation voltage a single curve may be used for a complete and adequate specification of X-ray quality. This may be contrasted with all other quality specifications, none of which is adequate without auxiliary information.

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I. INTRODUCTION

Numerous investigations during the past years have stressed the need for a more adequate filtration method of determining the quality of X-ray beams that are excited by different potential wave forms. It is not that the methods in use—such as the half-value layer—are theoretically unsound, but rather that, given alone, they are insufficient to give satisfactory correlation between radiations excited by potentials of different wave form. Furthermore, the several different methods in vogue do not express the quality of radiation in comparable terms.

It is, of course, well recognized that while the quality of an X-ray beam is given accurately only by the spectral energy distribution of the radiation, it is unfortunately impractical for common use. Accordingly, various indirect methods of quality description have been based upon the absorption properties of some metal such as copper or aluminum for the radiation in question. Since an X-ray spectrum is a function of the potential, these methods are frequently complicated by the fact that the potential used for exciting the X-rays is periodically fluctuating. The "simple spectrum" is one produced by, and a function of, the instantaneous or sustained value of the exciting voltage, and the target material.

[1] Presented at First American Congress of Radiology, Chicago, Ill., Sept. 25, 1933.

On the other hand, a "composite spectrum" is the resultant of the succession of instantaneous spectra produced by a periodically fluctuating potential and is, therefore, also a function of the wave form. Since the voltage wave forms applied to X-ray tubes are exceedingly varied and complicated, it is obvious that there is no direct simple relationship between the resultant composite spectra and the peak value of the exciting voltage. The absorption curve for radiation having a composite spectrum will be referred to as a "composite absorption curve" to distinguish it from the "simple absorption" curve characteristic of X-rays produced by constant potential.

Prime requisites for a satisfactory quality specification are, therefore: (1) A sound theoretical relationship between observed magnitudes and the spectral distribution of the radiation, and (2) a simple method of quality correlation which is reasonably independent of the exciting voltage wave form, i.e., a correlation between the quality of some one simple spectral distribution and that of the given composite spectral distribution. Simplicity and convenience of operation naturally dictate the choice of method only after these two requirements are satisfied.

Of the customary quality specifications: (1) Complete absorption curve,[2,3] (2) half-value layer,[4] (3) effective wave length,[5,6] and (4) average wave length [7]—Duane's effective wave-length method, requiring but two measurements, is the most convenient. This simplicity is offset, however, by the indefiniteness of the final result.[8] The half-value layer method has a slight advantage in simplicity over the remaining methods in that it requires fewer auxiliary computations. A theoretically definite conclusion, however, is obtained only from the complete absorption curve, the others requiring further information which can only be obtained from the complete absorption curve. That the complete absorption-curve method is not only adequate but has advantages not possessed by any of the others has been shown by a number of workers.[9] For example, Silberstein has shown [10] theoretically that a given X-ray spectral distribution will yield a particular copper absorption curve; and conversely, a spectral distribution which is sufficiently accurate for practical purposes may be derived from the complete copper absorption curve.

Until recently the complete absorption-curve method has had the disadvantage of not being expressible by a single numerical magnitude. This has been removed, however, by finding that,[11] within reasonably satisfactory limits, the complete composite absorption curve of radiation excited by any particular one of the different potential wave forms in use, may be matched by the simple absorption curve of the same material for radiation excited by some definite constant potential. It is further found [12] that such beams having equivalent absorption curves are, over a considerable range of initial filtration, closely alike as regards their intensity distribution in a large body of low atomic number material such as a water phantom. Since the

[2] E. A. Pohle and C. S. Wright, Radiology, vol. 14, p. 17, 1930.
[3] R. B. Wilsey, Radiology, vol. 17, p. 700, 1930.
[4] H. Holthusen and R. Braun, Strahlentherapie, vol. 47, p. 263, 1933.
[5] W. Duane, Proc. Nat. Acad., vol. 13, p. 668, 1927.
[6] L. S. Taylor, B.S. Jour. Research, vol. 5 (RP–212), p. 517, 1930.
[7] A. Mutscheller, Radiology, vol. 12, p. 283, 1929.
[8] E. Quimby, Am. Jour. Roent., vol. 21, p. 64, 1929. See also footnote 6.
[9] L. S. Taylor, G. Singer, and C. F. Stoneburner, B.S. Jour. Research, vol. 11 (RP–592), p. 293, 1933. See also footnotes 2 and 3.
[10] L. Silberstein, Phil. Mag., ser. 7, vol. 15, p. 375, 1933.
[11] See footnote 9.
[12] L. S. Taylor and K. L. Tucker, B.S. Jour. Research, vol. 9 (RP–475), p. 333, 1932.

spectral distribution of radiation excited by constant potential is perfectly reproducible, a family of simple absorption curves of constant voltage radiation should constitute a very convenient and adequate standard of reference for inferring the constant potential equivalent [13] of any given radiation.

It is of course obvious that two equivalent X-ray beams might be produced by voltages of very different peak values and hence one beam have shorter wave lengths not present at all in the other. However, the proved equivalence, where the peak voltages are very different, signifies that while there are some shorter wave lengths in one spectrum than in the other, they are present to a negligible extent.[14] As the equivalent constant voltage approaches the peak voltage, it signifies that the energy in the shorter wave lengths becomes relatively greater. This, however, is taken care of in the specification of quality by the fact that for a given peak voltage, if the shorter wave lengths gain in importance, the equivalent voltage is correspondingly increased. For example, with X-rays produced respectively by mechanical, full-wave, or Villard rectifiers operated at the same peak values, the equivalent voltage approaches nearer the peak value, indicating an increasing relative intensity of the shorter wave lengths. Correspondingly it is found that the absorption curves indicate, respectively, harder composite radiations after the same initial filtration.

It is also to be expected that two beams which yield like absorption curves with a low or moderate initial filtration (up to 1.5 mm Cu at 150 kv (constant)), may after a higher initial filtration furnish somewhat divergent curves—the curve for the radiation having the higher peak voltage falling above the other. By matching the curves above the point corresponding to the initial filtration, however, a new equivalent voltage may be found which specifies the radiation more closely. This is perfectly justifiable, since the radiation not passing through the filter is lost.

This specification of X-ray quality, by using the complete absorption curve, has been recommended by the X-ray standardization committee of the Radiological Society of North America.[15]

The main purpose, then, of the present investigation was to lay a general foundation and develop a procedure for deriving the two parameters of any absorption curve, namely, the equivalent constant potential excitation, together with the equivalent initial absorption.

II. EXPERIMENTAL PROCEDURE AND CORRELATION OF ABSORPTION CURVES

The standard absorption curves shown here were obtained under conditions believed to be adequate for the purpose at the present time. The irradiation [16] was measured in roentgens per minute by

[13] By "constant potential equivalent" is meant the constant potential necessary to apply to an X-ray tube to yield a simple absorption curve of the same form as the composite absorption curve in the same material for the unknown radiation in question.

[14] L. S. Taylor, G. Singer, and C. F. Stoneburner, B.S. Jour. Research, vol. 11 (RP-592), p. 293, 1933. In particular see curves in figs. 8 and 9 of this paper.

[15] Quotation from par. 7, 1933 committee report, "For most practical purposes the quality of the X-radiation may be satisfactorily specified in terms of the copper or aluminum absorption curve combined with a statement of the initial filtration. In lieu of an absorption curve, the equivalent constant potential applied to the tube terminals to yield the same curve may be stated as a single numerical magnitude. Up to 100 kv (constant) aluminum absorption curves and above 100 kv (constant) copper absorption curves shall be used to establish the equivalent potential."

[16] The term "irradiation" is used to emphasize the fact that these measurements were made in terms of the ionization produced in air. The ionization measurements can be used for "intensity" only when dealing with X-ray beams of exactly the same spectral distribution, but not with beams of different distribution.

means of a standard guarded field ionization chamber. The ionization current was measured by a null method [17] using an electrometer and compensating system previously described. The readings were accurate within ±0.3 percent. Voltages applied to the tube were supplied by a kenotron rectifier of the Hull-Webster type, in which at the tube currents used the ripplage did not exceed 1 percent.

The average tube voltage was measured by means of a shielded high-resistance voltmeter connected directly across the tube terminals.[18] The voltages given are all average values and hence peak values are about 0.3 to 0.5 percent higher. Since the average voltage has been shown to provide a better indication than peak voltage of the tube output on voltages of different ripplage,[19] the uncertainty of 0.2 percent in the peak value is of no consequence. During observations the tube voltage was measured and kept constant within limits of about 0.15 percent.

The X-ray tubes employed were housed in a lead box 4 by 4 by 7 feet. To provide steadiness of operation the filament was heated by a storage battery, and the high-voltage source supplied through a power stabilizer. Fluctuation in voltage was very slow, corresponding to, and caused by, the change in power line frequency; and, since it was seldom greater than about ±0.3 percent, was easily compensated manually.

The filters were located for convenience about 50 cm from the target and 60 cm from the entrant diaphragm on the chamber. This precluded the possibility of a measurable amount of scattered radiation entering the chamber. To further insure this, the beam was diaphragmed down to a diameter of about 4 cm at the filters.

Two types of tungsten target tube were used for the measurements—a hard glass thick-walled type for the higher excitation potentials and a soft glass thin-walled type for the lower—corresponding approximately to the voltage ranges in which such tubes are used in practice. Since absorption of radiation by the walls is very different between such tubes, it is necessary that it be taken into consideration. Of a number of thick pyrex tubes available we chose for the final measurements one 4.8 mm thick, about the average of the group.

Table 1 gives the copper absorption values for radiation from a thin tube (in which the wall absorption is about the same as for 0.02 mm of copper). In the first column are given filter thicknesses at selected intervals. In the other double columns headed by the applied tube voltage are given respectively the percent transmission of the filter and its corresponding logarithm to the base 10. Where, in making the measurements, the filter thickness or applied voltage deviated appreciably from the given rounded values, corrections were applied to obtain the desired values.

Similar data for the thick pyrex tube (having a wall absorption about the same as 0.1 mm of copper) is given in table 2.

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[17] L. S. Taylor, B.S.Jour. Research, vol. 6 (RP306), p. 807, 1931.
[18] L. S. Taylor, B.S.Jour. Research, vol. 5 (RP 217), p. 609, 1930.
[19] L. S. Taylor, G. Singer, and C. F. Stoneburner, B.S.Jour. Research, vol. 9 (RP 491), p. 561, 1932.

TABLE 1.—*Absorption of general X-radiation in copper*

Tube wall, 1.29 mm cerium glass

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	100 kv		110 kv		120 kv		130 kv		140 kv		150 kv	
	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
0.14	20.4_0	1.310	22.0_8	1.344	23.8_9	1.377	25.8_2	1.412	27.6_3	1.442	30.3_5	1.482
.20	15.3_9	1.187	17.8_4	1.251	19.9_3	1.299	21.8_1	1.339	23.4_2	1.370	25.6_8	1.410
.25	12.8_9	1.110	15.1_8	1.181	17.3_7	1.240	19.1_9	1.283	20.8_5	1.319	22.8_8	1.359
.30	11.1_5	1.047	13.1_7	1.120	15.2_8	1.183	17.0_9	1.230	18.7_1	1.267	20.5_8	1.313
.40	8.78	.943	10.2_8	1.012	12.1_3	1.084	13.7_5	1.138	15.3_7	1.187	16.9_3	1.230
.50	7.15	.854	8.50	.924	10.0_5	1.002	11.5_7	1.063	13.0_6	1.116	14.4_2	1.159
.75	4.53	.656	5.77	.761	7.04	.848	8.32	.920	9.55	.980	10.6_3	1.029
1.00	3.08	.489	4.13	.616	5.18	.714	6.35	.803	7.41	.870	8.43	.926
1.50	1.77	.248	2.42	.384	3.13	.496	4.00	.602	4.86	.687	5.75	.760
2.00	1.03	.013	1.60	.210	2.06	.314	2.73	.436	3.38	.529	4.13	.616
2.50	------	------	1.02	.009	1.46	.164	2.00	.301	2.50	.398	3.12	.494
3.00	------	------	------	------	1.09	.037	1.48	.170	1.93	.286	2.49	.396

TABLE 2.—*Absorption of general X-radiation in copper*

Tube wall, 4.78 mm pyrex glass

I_o≡Incident radiation. I≡Transmitted radiation. 100 I/I_o= Percent transmission.

Copper filter	100 kv		110 kv		120 kv		130 kv		140 kv		150 kv		160 kv		170 kv		180 kv	
	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o
mm																		
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
.14	44.3$_9$	1.646	46.2$_8$	1.665	49.6$_0$	1.695	52.1$_8$	1.717	54.2$_0$	1.734	55.6$_8$	1.745	56.6$_3$	1.753	57.9$_5$	1.763	59.5$_6$	1.775
.20	34.5$_9$	1.539	37.0$_0$	1.568	40.7$_2$	1.610	43.9$_0$	1.642	45.2$_5$	1.656	47.2$_0$	1.674	49.0$_0$	1.690	51.1$_0$	1.708	52.8$_5$	1.723
.25	29.8$_8$	1.475	32.3$_9$	1.510	36.0$_0$	1.558	39.0$_8$	1.592	40.5$_0$	1.607	42.7$_0$	1.630	44.4$_5$	1.648	46.7$_5$	1.670	48.1$_8$	1.683
.30	25.8$_0$	1.411	28.6$_2$	1.457	32.3$_5$	1.510	34.0$_0$	1.531	36.9$_2$	1.567	38.6$_3$	1.587	40.6$_0$	1.609	42.8$_8$	1.632	43.9$_8$	1.643
.40	20.3$_5$	1.309	23.1$_8$	1.365	26.5$_6$	1.424	29.2$_0$	1.465	31.5$_5$	1.499	33.2$_8$	1.522	34.9$_5$	1.543	36.7$_5$	1.565	38.8$_7$	1.590
.50	16.3$_7$	1.214	18.9$_5$	1.278	21.8$_2$	1.339	24.3$_5$	1.387	26.7$_7$	1.428	29.3$_0$	1.467	30.1$_7$	1.480	32.1$_5$	1.507	33.8$_8$	1.530
.75	11.6$_0$	1.064	13.9$_2$	1.144	15.8$_2$	1.199	18.2$_8$	1.262	20.4$_1$	1.310	22.4$_0$	1.350	24.0$_3$	1.381	26.0$_4$	1.416	27.7$_2$	1.443
1.00	8.27	.918	10.2$_7$	1.012	11.9$_8$	1.078	14.0$_5$	1.148	16.0$_2$	1.205	17.8$_8$	1.252	19.5$_5$	1.291	21.2$_2$	1.327	22.7$_8$	1.358
1.50	4.44	.647	6.02	.780	7.68	.885	9.28	.968	10.8$_2$	1.034	12.2$_8$	1.089	13.8$_5$	1.141	15.2$_3$	1.182	16.4$_9$	1.217
2.00	2.60	.415	3.89	.590	5.17	.714	6.53	.815	7.78	.891	9.02	.955	10.1$_8$	1.008	11.4$_3$	1.058	12.6$_3$	1.103
2.50	------	------	------	------	3.55	.550	4.67	.669	5.87	.769	6.84	.835	7.88	.897	8.83	.946	9.95	.997
3.00	------	------	------	------	2.57	.410	3.61	.558	4.64	.667	5.54	.744	6.48	.812	7.36	.867	8.35	.921

TABLE 3.—*Absorption of general X-radiation in aluminum*

Tube wall, 1.29 mm cerium glass

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	60 kv		70 kv		80 kv		90 kv		100 kv		110 kv	
	$100\ I/I_o$	$\text{Log}\ 100\ I/I_o$	$100\ I/I_o$	$\text{Log}\ 100\ I/I_o$	$100\ I/I_o$	$\text{Log}\ 100\ I/I_o$	$100\ I/I_o$	$\text{Log}\ 100\ I/I_o$	$100\ I/I_o$	$\text{Log}\ 100\ I/I_o$	$100\ I/I_o$	$\text{Log}\ 100\ I/I_o$
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
1	32.1	1.507	33.8	1.530	36.0	1.557	38.9	1.590	40.3	1.606	42.4	1.628
2	19.0	1.279	20.8	1.318	22.9	1.360	25.2	1.403	27.2	1.435	29.4	1.468
3	12.8	1.109	14.4	1.158	16.5	1.218	18.4	1.265	20.3	1.309	22.3	1.349
4	9.3	.970	10.7	1.033	12.6	1.102	14.4	1.159	16.2	1.210	18.0	1.156
5	7.0	.845	8.44	.926	10.0	1.003	11.6	1.064	13.4	1.127	15.0	1.177
6	5.41	.733	6.79	.832	8.25	.916	9.69	.986	11.3	1.054	12.8	1.110
7	4.35	.639	5.53	.743	6.88	.838	8.33	.921	9.80	.991	11.2	1.050
8	3.55	.550	4.61	.664	5.84	.766	7.21	.858	8.58	.934	9.92	.997
10	2.44	.387	3.42	.534	4.38	.642	5.44	.736	6.63	.822	7.85	.895
15	1.16	.065	1.79	.253	2.40	.380	3.17	.501	4.06	.609	4.80	.681
20	-------	-------	1.00	.000	1.40	.147	2.01	.303	2.60	.415	3.17	.501

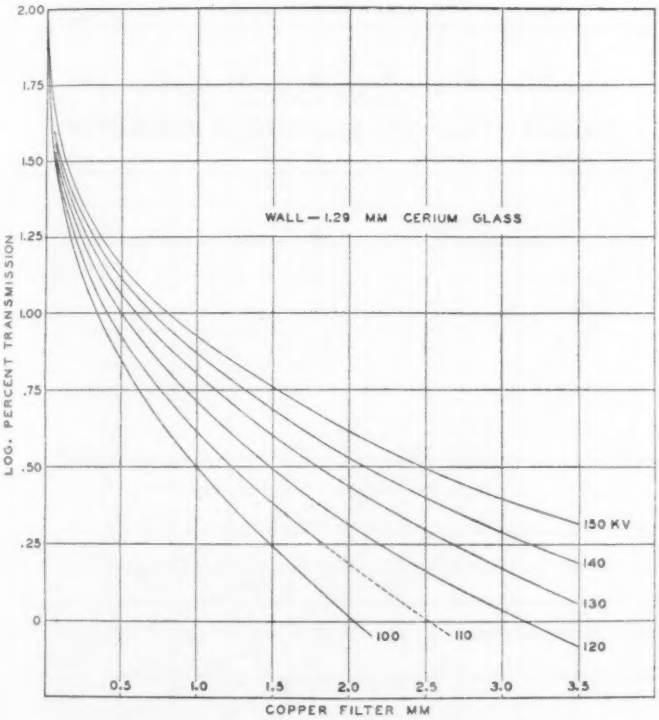

FIGURE 1.—*Copper absorption curves for thin glass tube.*

Below 100 kv (constant), absorption in aluminum has been recommended as a standard, hence table 3 gives aluminum absorption data. In making these measurements the same thin glass tube as for table 1 was used.

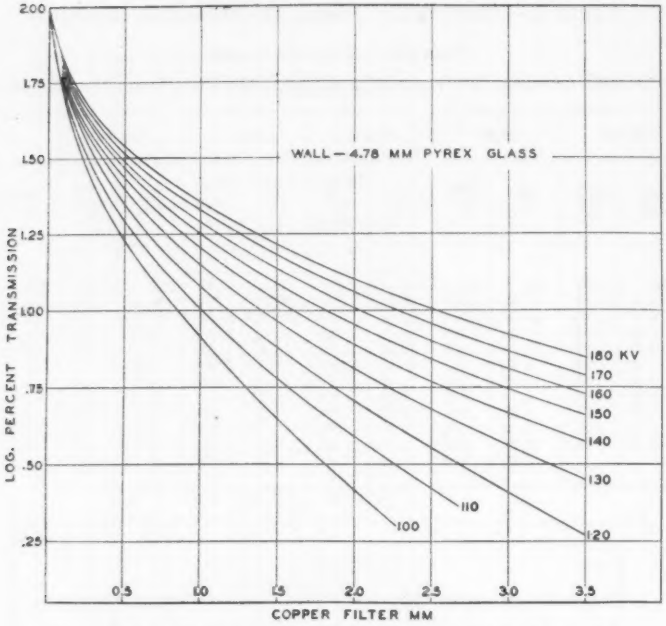

FIGURE 2.—*Copper absorption curves for thick glass tube.*

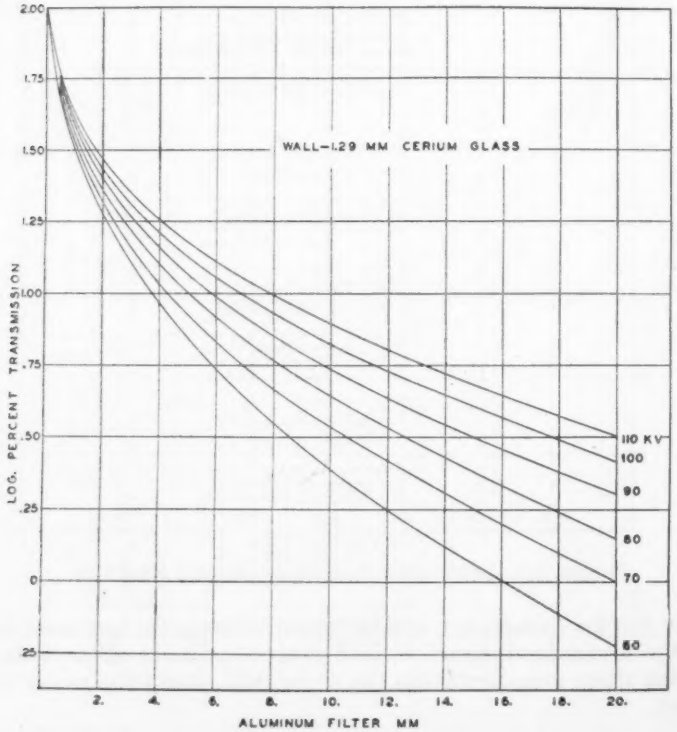

FIGURE 3.—*Aluminum absorption curves for thin glass tube.*

Figures 1, 2, and 3 give, respectively, for various constant potential excitations, the semilogarithmic absorption curves for copper and aluminum as plotted from tables 1, 2, or 3, respectively. If it is assumed that, for the same excitation potential, the spectral distribution of the radiation emitted by the anticathodes of the 2 tubes is the same, then the difference between the copper absorption curves corresponding to the same potential in figures 1 and 2 arises entirely from the difference in the absorption of the 2-tube walls—1.3-mm cerium glass, and 4.8-mm pyrex glass.

To bring out the general information to be inferred from the absorption curves of figures 1 to 3, and from this to correlate the curves of figure 2 with those of figure 1, we will take a hypothetical absorp-

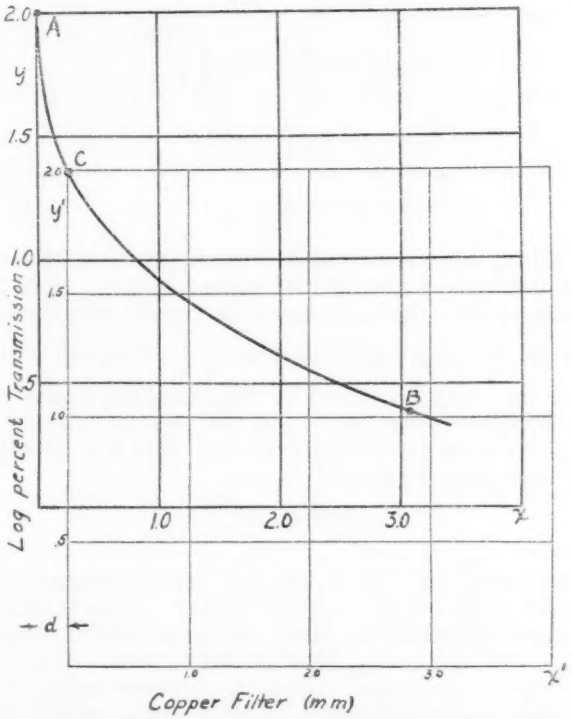

FIGURE 4.—*Hypothetical absorption curve showing the shift of coordinates due to initial filtration.*

tion curve AB (fig. 4) in which x gives the thickness of copper filter, and

$$y = \log\ (100\ I/I_o) \tag{1}$$

gives the corresponding values of log percent transmission. Here we will also assume that the incident radiation I_o is obtained from an ideal X-ray tube of zero wall thickness. In that case, AB is the basic absorption curve corresponding to the given excitation potential.

As a first case, we wish to show how, from this basic curve, the absorption curve is obtained for the same radiation after it has been modified in quality by traversing a given thickness, d, of the filter. In this case, I_d, the number of roentgens emerging from the thickness,

d, becomes the incident radiation for the new curve. Against new thickness values,

$$x' = x - d \tag{2}$$

of the filter, are plotted new log percent transmissions,

$$\begin{aligned} y' &= \log\left(100\frac{I}{I_d}\right) \\ &= \log\left(\frac{100\dfrac{I}{I_o}}{100\dfrac{I_d}{I_o}}\right) \\ &= \log\left(100\frac{I}{I_o}\right) + \log\left(\frac{100}{100\dfrac{I_d}{I_o}}\right) \\ &= y + 2 - \log\left(100\frac{I_d}{I_o}\right) \qquad (3) \\ &= y + \text{constant}. \end{aligned}$$

Thus all points on the new curve differ in position from corresponding ones on the basic curve by the same amount; that is, the new curve is obtained from the basic curve by merely shifting the origin of coordinates to the point $x=d$ and $y=-\left(2-\log 100\frac{I_d}{I_o}\right)$. That this conclusion is true may be shown by the following analysis. The 100 percent transmission point ($y'=2$) of the new curve must lie directly above the point $x=d$ on the basic curve; this is C in figure 4. By assigning y' this value in eq. 3

$$y = \log 100\frac{I_d}{I_o}$$

which is, compared with eq. 1, the log percent transmission on the basic curve for a thickness $x=d$ of the filter. This is consistent with the imposed condition that I_d should be considered the incident radiation for this particular case. If, then, we have the data for the basic absorption curve—no initial filtration—corresponding data for the radiation, after being subjected to any given initial filtration, is readily obtained by reducing the observed filter thicknesses by the initial thickness d, and by increasing all observed log percent transmissions by $2-\log\left(100\frac{I_d}{I_o}\right)$.

The second case deals with the converse problem: given two absorption curves of the same radiation, but subjected to different amounts of filtration; to find the difference in thickness of the initial filters. Here we are supposed to have two separate absorption curves of figure 4—AB on the xy axes; and CB plotted (on transparent paper) on the $x'y'$ axes. The second is laid over the first and shifted to that position where it is found to fit the first. The difference, d, in the two filter thicknesses, for corresponding points on the two curves, is

given by the difference $(x-x')$ for the point C and is the magnitude sought.

Having outlined the general procedure we shall next inquire if like excitation potentials in the two tubes of figures 1 and 2 produce absorption curves which are subject to the same correlation as curves CB and AB (fig. 4) just treated. In other words: is the radiation from the thick-wall pyrex tube (of fig. 2) of the same quality as that from the thin-wall tube (of fig. 1) after passing through some unknown thickness of copper?

By taking curves of figure 2 and fitting them, as just described, to the curves of like excitation potential in figure 1, a very satisfactory correlation is obtained. The curves of figure 5 are those of figure 1

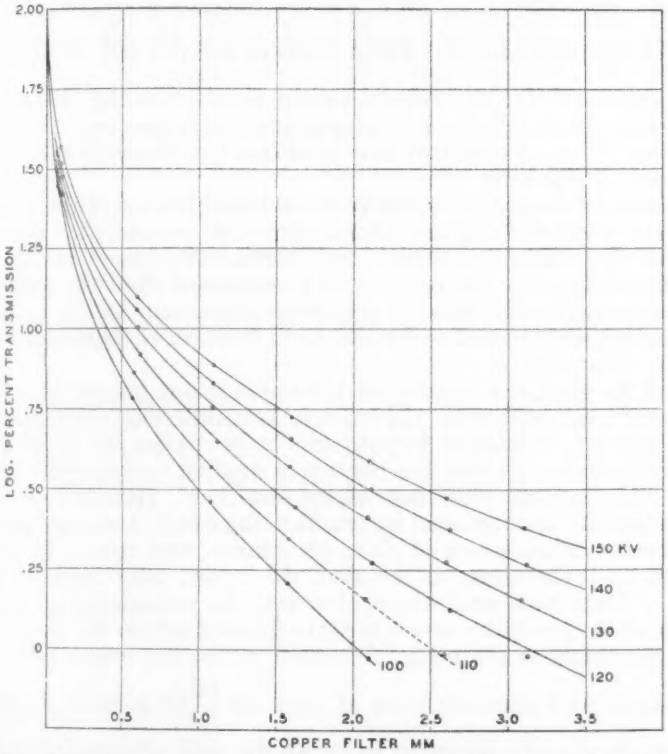

FIGURE 5.—*Copper absorption curves for thin tube (line) and thick tube (circles) superposed to show matching.*

reproduced; the plotted points on these curves are from the corresponding curves of figure 2—each point on the extreme left indicating the thickness of copper (about 0.1 mm) which would make up the difference in effect of the walls of the two tubes. As may be expected, this thickness varies somewhat with the excitation potential, because the spectral absorption in glass is not the same as in copper.

From the consistency of this correlation—in which it is obvious that absorption curves corresponding to different excitation potentials do not fit—it is to be concluded that the shape of the absorption curve is characteristic of the excitation potential. On the other hand, the coordinate displacement of the given curve from that of the basic

curve is characteristic of the filtration between the target and the point of measurement. Having a family of such curves (as in fig. 1), in which the constant excitation potential varies by steps of practicable magnitude, it is clear that instead of using the complete absorption curve to specify the quality of the radiation, we may use the more convenient magnitudes: excitation potential (constant) and initial filtration. Since, as shown in an earlier publication, the radiation from various wave forms of excitation potential may be simply and adequately equated to that of some equivalent constant potential excitation, the quality of any given radiation may be specified by its equivalent constant excitation potential and the initial filtration. This initial filtration is desirably expressed in terms of the equivalent copper or aluminum.

III. EQUIVALENT THICKNESS OF TUBE WALLS

This section is for the two-fold purpose of revealing the degree of consistency obtainable from the foregoing conclusion and of providing data from which an operator may evaluate the absorption in the wall of his own X-ray tube.

It should, of course, be borne in mind that because of the difference in atomic numbers of glass, aluminum, and copper, the equivalent thickness of one in terms of any other varies with the excitation potential of the radiation. By equivalent thickness of the tube wall, therefore, is meant the thickness of copper or aluminum which will reduce the given incident radiation by the same fraction of its initial value as does the tube wall.

As will be seen, the equivalent thickness is not proportional to the thickness of the material. Then, too, two different materials of the same equivalent thickness do not necessarily change the quality of the beam to the same degree; the change in quality varies with the exciting potential and the thickness of the absorber. However, for conditions ordinarily encountered in practice the quality change produced by equivalent thicknesses of glass, aluminum, and copper is not very different and therefore, as we shall do below, may usually be neglected. Thus tube wall absorption may be considered as a special example of the general case set forth in figure 4 where the wall absorption corresponds to the initial filtration, d, for the curve CB. Upon the experimental determination of $\log\left(100\frac{I_d}{I_o}\right)$ it is thus possible by the methods already discussed to set up the basic absorption curve for filter thickness greater than d—but not less.

Tables 4 to 10, inclusive, give absorption data for various tube walls, together with the commonly used filters of copper and aluminum.

TABLE 4.—*Absorption of general X-radiation in copper*

Initial filtration: Tube wall, 1.29 mm cerium glass and 0.25 mm copper

$I_o \equiv$Incident radiation. $I \equiv$Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	100 kv		110 kv		120 kv		130 kv		140 kv		150 kv	
	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
.15	66.5	1.823	67.3	1.828	69.8	1.844	71.8	1.856	73.5	1.866	74.5	1.872
.25	53.7	1.730	56.2	1.750	58.5	1.767	61.0	1.785	62.4	1.795	63.8	1.805
.5	34.2	1.534	38.0	1.580	40.7	1.609	43.7	1.640	45.7	1.660	47.1	1.673
.75	23.9	1.378	27.2	1.435	29.8	1.475	33.1	1.520	35.5	1.551	36.9	1.567
1.25	13.7	1.138	15.9	1.203	18.0	1.256	20.9	1.319	23.3	1.368	25.2	1.401
1.75	8.00	.903	10.1	1.005	11.9	1.074	14.2	1.154	16.2	1.210	18.1	1.257
2.25	------	------	6.70	.826	8.40	.924	10.4	1.018	12.00	1.078	13.7	1.136
2.75	------	------	------	------	6.11	.786	7.72	.887	9.25	.966	10.9	1.037

TABLE 5.—*Absorption of general X-radiation in copper*

Initial filtration: Tube wall, 1.29 mm cerium glass, and 0.5 mm copper

$I_o \equiv$Incident radiation. $I \equiv$Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	100 kv		110 kv		120 kv		130 kv		140 kv		150 kv	
	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o	100 I/I_o	Log 100 I/I_o
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
.25	63.8	1.805	67.6	1.830	70.2	1.846	71.8	1.856	73.3	1.865	74.6	1.873
.50	44.3	1.646	48.7	1.688	51.6	1.712	54.9	1.739	56.8	1.754	58.5	1.767
1.0	24.4	1.387	28.5	1.455	31.2	1.494	34.6	1.539	37.2	1.571	39.9	1.601
1.5	14.6	1.165	18.1	1.257	20.5	1.312	23.6	1.373	25.9	1.413	28.6	1.457
2.0	9.29	.968	12.0	1.080	14.5	1.162	17.3	1.238	19.1	1.280	21.6	1.335
2.5	------	------	------	------	10.9	1.035	12.8	1.107	14.8	1.170	17.3	1.237

TABLE 6.—*Absorption of general X-radiation in copper*

Initial filtration: Tube wall, 1.29 mm pyrex glass, and 0.25 mm pyrex

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	100 kv		110 kv		120 kv		130 kv		140 kv		150 kv		160 kv		170 kv		180 kv	
	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$
mm																		
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
.15	68.6	1.836	70.5	1.848	72.1	1.858	74.2	1.870	75.9	1.880	77.3	1.888	78.3	1.894	79.3	1.899	80.2	1.904
.25	57.3	1.758	59.6	1.775	61.7	1.790	63.5	1.803	66.1	1.820	67.9	1.832	68.9	1.838	70.0	1.845	71.4	1.854
.50	38.8	1.589	42.2	1.625	43.9	1.643	46.8	1.670	50.4	1.702	52.5	1.720	54.1	1.730	55.1	1.741	57.6	1.760
.75	27.7	1.442	31.3	1.495	33.3	1.522	35.9	1.556	39.6	1.597	41.9	1.622	44.0	1.643	45.4	1.657	47.3	1.675
1.25	14.9	1.172	18.6	1.269	21.3	1.330	23.7	1.376	26.7	1.426	28.8	1.459	31.3	1.496	32.6	1.513	34.2	1.534
1.75	8.70	.940	12.00	1.079	14.4	1.157	16.7	1.223	19.2	1.284	21.1	1.325	22.9	1.360	24.4	1.388	26.3	1.420
2.25	----------	----------	7.96	.900	9.87	.994	11.9	1.076	14.5	1.161	16.0	1.205	17.7	1.249	19.3	1.285	21.3	1.328
2.75	----------	----------	----------	----------	7.14	.854	9.24	.966	11.5	1.059	13.0	1.113	14.6	1.164	15.8	1.197	17.3	1.239

TABLE 7.—*Absorption of general X-radiation in copper*

Initial filtration: Tube wall, 4.78 mm pyrex glass, and 0.5 mm copper

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	100 kv		110 kv		120 kv		130 kv		140 kv		150 kv		160 kv		170 kv		180 kv	
	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$
mm																		
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
.25	70.2	1.846	71.5	1.854	73.3	1.865	75.0	1.875	76.6	1.884	78.5	1.895	79.6	1.901	80.9	1.908	82.0	1.914
.50	50.1	1.700	53.2	1.726	55.4	1.743	57.7	1.761	60.0	1.778	62.4	1.795	64.3	1.808	66.1	1.820	67.5	1.829
1.00	27.1	1.433	31.8	1.502	35.2	1.546	38.1	1.581	40.1	1.603	43.0	1.633	45.3	1.656	47.3	1.675	48.6	1.687
1.50	15.9	1.201	20.5	1.312	23.6	1.373	26.8	1.429	29.1	1.463	31.5	1.499	33.7	1.528	35.6	1.551	37.4	1.573
2.00	----------	----------	----------	----------	16.3	1.211	19.5	1.290	21.9	1.341	23.9	1.379	26.1	1.417	28.2	1.450	29.9	1.476
2.50	----------	----------	----------	----------	11.8	1.071	14.8	1.171	17.3	1.239	19.1	1.280	20.9	1.320	22.9	1.360	24.6	1.392

TABLE 8.—*Absorption of general X-radiation in aluminum*

[Initial filtration: Tube wall, 1.29 mm cerium glass, and 1.0 mm aluminum]

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	60 kv		70 kv		80 kv		90 kv		100 kv		110 kv	
	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
1	59.2	1.772	61.5	1.789	63.6	1.803	64.9	1.813	67.4	1.829	69.3	1.841
2	40.0	1.602	42.5	1.629	45.8	1.661	47.3	1.675	50.4	1.703	52.6	1.721
3	29.1	1.464	31.8	1.503	35.1	1.545	37.0	1.569	40.1	1.603	42.5	1.628
4	21.8	1.338	24.9	1.397	28.0	1.447	29.8	1.475	33.2	1.521	35.4	1.549
5	16.8	1.226	20.4	1.310	22.9	1.360	24.9	1.397	28.0	1.448	30.3	1.482
6	13.5	1.131	16.3	1.213	19.1	1.281	21.4	1.331	24.3	1.385	26.4	1.422
7	11.1	1.043	13.6	1.134	16.2	1.210	18.5	1.268	21.2	1.327	23.4	1.369
9	7.59	.880	10.1	1.004	12.2	1.085	14.0	1.146	16.4	1.215	18.5	1.267
14	3.61	.557	5.28	.723	6.66	.824	8.15	.911	10.0	1.001	11.3	1.054
19	1.86	.271	2.95	.470	3.89	.590	5.16	.713	6.44	.809	7.47	.873

TABLE 9.—*Absorption of general X-radiation in aluminum*

[Initial filtration: Tube wall, 1.29 mm cerium glass, and 2.0 mm aluminum]

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	60 kv		70 kv		80 kv		90 kv		100 kv		110 kv	
	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
1	67.5	1.829	69.2	1.840	72.0	1.858	72.9	1.863	74.9	1.875	76.0	1.881
2	49.1	1.691	51.8	1.714	55.1	1.741	57.0	1.756	59.6	1.775	61.3	1.787
3	36.8	1.566	40.5	1.608	43.9	1.263	45.9	1.661	49.3	1.693	51.1	1.708
4	28.4	1.454	32.6	1.514	36.0	1.556	38.3	1.584	41.6	1.619	43.8	1.642
5	22.9	1.360	26.6	1.424	30.0	1.477	33.0	1.518	36.0	1.557	38.2	1.582
6	18.7	1.271	22.2	1.345	25.5	1.406	28.5	1.455	31.5	1.499	33.7	1.528
8	12.8	1.103	16.4	1.216	19.1	1.281	21.5	1.333	24.8	1.394	26.7	1.427
13	6.10	.785	8.60	.935	10.5	1.020	12.6	1.099	14.9	1.174	16.3	1.213
18	3.15	.498	4.80	.681	6.12	.787	7.96	.901	9.56	.981	10.8	1.033

TABLE 10.—*Absorption of general X-radiation in aluminum*

[Initial filtration: Tube wall, 1.29 mm cerium glass, and 4.0 mm aluminum]

I_o≡Incident radiation. I≡Transmitted radiation. $100\ I/I_o$=Percent transmission.

Copper filter	60 kv		70 kv		80 kv		90 kv		100 kv		110 kv	
	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$	$100\ I/I_o$	Log $100\ I/I_o$
mm												
0	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00	100	2.00
1	75.0	1.875	78.3	1.894	79.8	1.902	80.4	1.905	82.6	1.917	83.3	1.921
2	57.9	1.763	63.0	1.799	65.3	1.815	67.2	1.828	69.8	1.839	71.4	1.854
3	46.6	1.668	51.3	1.710	54.4	1.736	57.8	1.762	60.5	1.782	62.2	1.794
4	38.0	1.580	42.8	1.631	46.2	1.665	50.0	1.699	53.0	1.724	55.0	1.741
6	26.1	1.417	31.7	1.501	34.7	1.540	37.7	1.577	40.9	1.612	43.6	1.639
11	12.4	1.094	16.6	1.220	19.0	1.279	22.0	1.342	25.1	1.399	26.6	1.425
16	6.42	.807	9.28	.968	11.1	1.046	14.0	1.145	16.5	1.218	17.6	1.245

Samples used for obtaining absorption data (tables 11 and 12) of tube walls were in part cut from old tubes and in part from unused plane plates of lime and pyrex glass. The thickness of the curved pieces was measured by a spherical micrometer. The wall thickness, D, of the X-ray tubes used was also measured—by the customary micrometer microscope method—focussing first on the outer surface markings, then on the inner surface markings, and observing the displacement, s, of the microscope between these two positions.[20] This displacement multiplied by the refractive index, n, of the glass gives its thickness. The index of refraction used for lime glass was 1.52 and that for pyrex 1.48.[21] These refractive indices were checked by thickness measurements, D, and displacement measurements, s, on pieces of the same kind from broken tubes, n being equal to D/s.

TABLE 11.—*Copper and aluminum equivalents of pyrex glass for radiations excited by various constant potentials and filtered by 1.3 mm of cerium glass (copper equivalence, about 0.02 mm)*

Thickness of pyrex	100 kv			110 kv			120 kv			130 kv		150 kv	
	Log % transmission	Cu thickness	Al thickness	Log % transmission	Cu thickness	Al thickness	Log % transmission	Cu thickness	Al thickness	Log % transmission	Cu thickness	Log % transmission	Cu thickness
mm		*mm*	*mm*		*mm*	*mm*		*mm*	*mm*		*mm*		*mm*
0	2.00	0	0	2.00	0	0	2.00	0	0	2.00	0	2.00	0
2	1.657	.02	.80	1.667	.025	.95	1.720	.025	1.05	1.756	.023	1.804	.024
4	1.477	.067	2.10	1.508	.064	2.15	1.539	.066	2.22	1.604	.065	1.640	.070
6	1.354	.115	3.52	1.382	.117	3.70	1.405	.125	3.80	1.459	.125	1.512	.124
8	1.265	.157	5.00	1.301	.167	4.70	1.330	.175	5.25	1.362	.180	1.428	.180
10	1.176	.205	5.95	1.225	.22	6.15	1.258	.23	6.6	1.292	.237	1.356	.245
12	1.079	.260	7.25	1.146	.28	7.40	1.182	.30	7.9	1.225	.30	1.288	.32

For determining the copper and aluminum absorption equivalents of pyrex glass above 100 kv, table 11, the radiation from the cerium glass tube of figure 1 was used, being taken without wall correction as representing the unaltered anticathode radiation. This was considered permissible in that the copper equivalent of its wall could not be more than 0.02 mm—one sixth that found for the difference between this thin tube and the pyrex tube of figure 2.

For determining the aluminum equivalents of lime glass, table 12, a lime glass tube, 0.45 mm thick, was used as source of radiation. The nearly linear relation between the thicknesses of glass and of aluminum which have the same absorption at the lower thicknesses permits a fairly accurate aluminum equivalent to be assigned to this tube wall.[22]

An examination of tables 11 and 12 will show that the variation with exciting voltage of the equivalent copper or aluminum filtration of glass is not large and may be assumed as constant except for the most accurate work.

The consistency of these data on tube wall equivalents is strikingly illustrated in figure 6 by the accuracy of the correlation which they furnish for the copper absorption curves of the radiation from 5 tubes differing both in construction and wall thickness, all excited by 150 kv (constant).

[20] The surface markings are best seen under tangential illumination.
[21] Their respective densities were 2.54 and 2.24.
[22] There may be some question as to the validity of this assumption since the measurements were all made on a radiation initially filtered with 0.45 mm of lime glass. If present at all, the error is small.

TABLE 12.—*Aluminum equivalents of lime glass for radiations excited by various constant potentials and filtered by 0.45 mm of lime glass*

Thickness of lime glass	60 kv		80 kv		100 kv	
	Log % transmission	Al thickness	Log % transmission	Al thickness	Log % transmission	Al thickness
mm		*mm*		*mm*		*mm*
0	2.00	0	2.00	0	2.00	0
.5	1.607	.42	1.690	.47	1.751	.48
1.0	1.516	.84	1.558	.86	1.605	.88
1.5	1.403	1.26	1.461	1.30	1.526	1.33
2.0	1.295	1.72	1.373	1.76	1.459	1.78
2.5	1.185	2.16	1.286	2.23	1.395	2.24
3.0	1.072	2.56	1.199	2.74	1.322	2.77

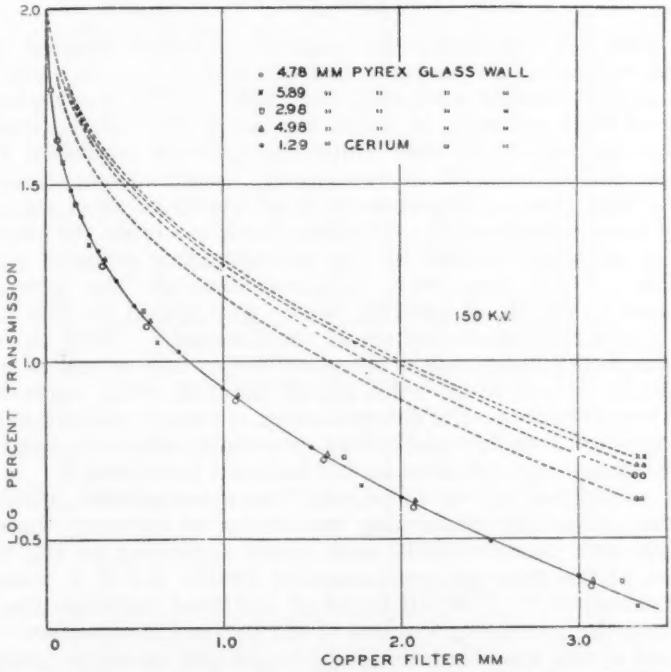

FIGURE 6.—*Absorption curves showing the correction for wall effect.*

To be properly related, the data for these curves should be plotted each on its proper coordinates as fixed by the wall filtration. To avoid this multiplicity of coordinate systems, the data for the pyrex tubes (dash lines) and the cerium tube (solid line) are plotted in the usual manner taking as 100 percent transmission, the radiation filtered only by the tube wall in each case. Finally, the data for all pyrex tubes are correlated with that of the cerium glass tube, following the procedure indicated by equations 2 and 3 and taking into account here the copper equivalent of the cerium tube wall. All copper filtration values for the pyrex tube data are increased by the difference in the copper equivalents of the two tube walls—that of the cerium tube being estimated as .02 mm of Cu. All log percent transmissions

for the radiation from the pyrex tube are accordingly decreased by the difference in the log percent transmission of the corresponding copper equivalents of the walls—as given in table 11. This operation should bring the absorption curve for the given pyrex tube into coincidence with that of the cerium tube. This correlation is indicated by the plotted points on the full line curve for the cerium tube of figure 6.

The fit is very good, and shows with what assurance the quality of constant potential radiation from a tube of given wall thickness can be evaluated in terms of the constant potential excitation and equivalent filtration. In other words, the equivalent thickness of the tube wall constitutes a unique and adequate specification of the quality of radiation furnished by a given X-ray tube.

IV. COPPER ABSORPTION CURVES ABOVE 250 KV EXCITATION POTENTIAL

The need for specifying the quality of X-rays excited by the so-called "ultra-high voltages"—250 kv and above—is particularly accentuated at present when such radiations are fast coming into use. In case of such radiation in which the wave form of the excitation potential varying as it does from the extreme furnished by the induction coil up to that of very nearly constant magnitude, it is essential that their equivalence be fixed—perhaps most suitably in terms of constant potential. The first step is to obtain the absorption curves of radiation excited by the corresponding range of constant potentials. These data were obtained through the courtesy of Dr. Roscoe L. Smith, of Lincoln, Nebr., who placed for this purpose his 800-kv constant-potential set at our disposal.[23] With this set, in which the X-ray tube with a tungsten target had a wall of 6.4-mm steel plus 13 mm of water—this initial filtration being equivalent to about 6 mm of copper—the determination of copper absorption curves in the range between 250 and 550 kv (constant) was carried out under as nearly standard conditions as the facilities permitted.[24]

Since, as pointed out by Lauritsen,[25] the international definition of the roentgen permits disturbing conditions to enter at these high potentials, our measurements were made according to the revised definition of the roentgen recommended by the R.S.N.A. standardization committee.[26] Here all forms of scattered radiation are eliminated from the measuring volume of the ionization chamber.

The end of the tube containing the target and its water jacket was surrounded by a lead shield 1 inch thick, in which a hole about ¾ inch in diameter was drilled to serve as a window for passing the radiation. The filters were inserted in the beam immediately adjacent to the lead cap; and the limiting diaphragm for the ionization chamber placed 35 cm from these. This diaphragm consisted of a 2.5-cm square hole half way out on the radius of a large circular lead disk 2.54 cm thick. Following the technique described by Lauritsen the beam was cut off, without altering the amount of extraneous radiation entering the ionization chamber, by rotating this lead disk on its geometrical axis. The difference in reading of the ionization chamber magnitude

[23] We are greatly indebted to him and to Mr. T. R. Folsom for their cordial cooperation and assistance.
[24] Only a brief description of these is given here, as others will undoubtedly publish a more adequate one.
[25] C. C. Lauritsen, Am. Jour. Roentgenology, vol. 6, p. 321, 1933.
[26] "The roentgen is the quantity of X-radiation which, when the secondary electrons are fully utilized and the effects of all scattered radiation avoided, produces in 1 cubic centimeter of atmospheric air at O C and 76-cm mercury pressure, such a degree of conductivity that one esu of charge is measured under saturation conditions."

with the limiting diaphragm open and closed eliminated the effect of radiation scattered from the room.

The ionization chamber was of the parallel aluminum plate type, having a 28-cm spacing between the plates. That this separation was probably sufficient, at the voltages used, is concluded from cloud expansion photographs [27] which show that at a considerably higher peak voltage the bulk of the ion tracks are confined within 10 cm of the sides of the beam.

The ionization current was measured by a high sensitivity galvanometer, and voltages by the spark gap between 50-cm spheres placed

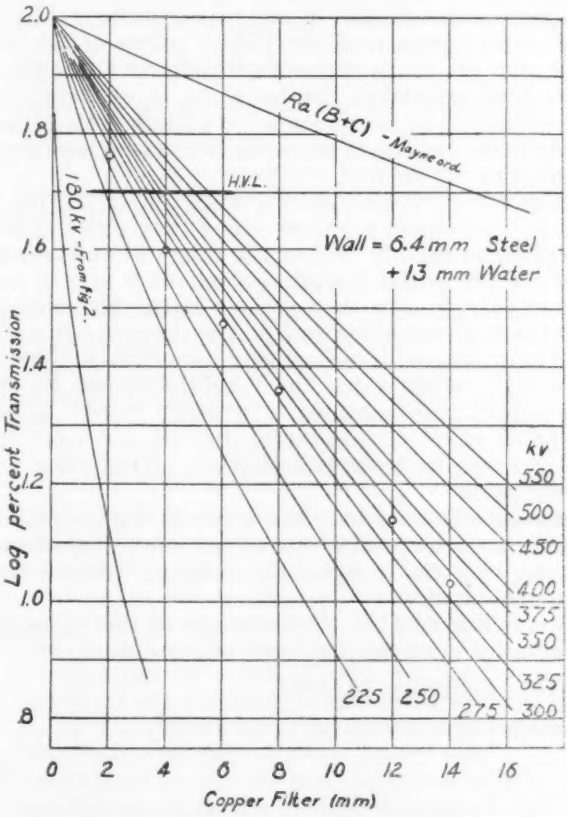

FIGURE 7.—*Copper absorption curves above 225 kv; voltages are peak values which are the same as the effective values within the limits of error of measurement.*

in accordance with 1928 AIEE standards and corrected to normal pressure. These potential measurements were in reasonably close agreement with the sum of the potentials measured individually on each of the cascaded units by the manufacturer.

The resulting semilogarithmic copper absorption curves, for the indicated excitation potentials and an initial filtration equivalent to about 6 mm of copper, are plotted in figure 7. Along with these is also plotted the curve for radiation excited by 180 kv (constant) and

[27] C. C. Lauritsen, personal communication.

initially filtered by 4.8 mm of pyrex glass—equivalent to 0.1 mm of copper—that obtained by Mayneord [28] for 370 kv (constant), but an unstated initial filtration; and, of radiation from a sample of Ra (B+C) after "a heavy" initial filtration (also from Mayneord). The half-value layer line is also inscribed at $\log_{10} 50 = 1.70$.

Owing to the very different excitation potentials and intitial filtrations involved in radiations of figure 7, as compared with those of figures 1 and 2, no attempt is made to correlate the absorption curves of figure 6 with the basic curves of figure 1.

For the 370-kv (constant) curve of Mayneord the initial filtration was confined to the tube wall and hence was of much smaller copper value than that (about 6 mm) in our measurements. In this respect Mayneord's curve agrees with our 374-kv curve at the lower copper filtrations in that his drops the more rapidly as it should; but at the highest filtrations somewhat greater slope of our curve denies the agreement. Since his measurements were made with a thimble chamber of unknown wall effect, it seems rather gratifying that the results are not even more divergent.

Inasmuch as our curves of figure 7 were obtained with nearly constant potential—2 percent ripplage—they may serve as standard for specifying radiation quality within the range of excitation potentials covered and for the initial filtration of about 6 mm of copper. Absorption curves obtained with a greater initial filtration can be correlated with these curves of figure 7 just as those of figure 2 with figure 1; but not so with curves for radiation of lower initial filtration because of the uncertainty with which the magnitudes can be extrapolated toward the higher transmissions. In other words, although these curves can be of value as standards, they do not have the range of application reserved to basic curves—i.e., of radiation subjected to zero initial filtration.

We would suggest, therefore, that in specifying the radiation in this high potential range the peak of the excitation voltage be stated when possible along with the equivalent constant voltage until further studies have been made.

Recognition is due to C. F. Stoneburner of this laboratory for his valuable assistance in obtaining much of the data.

WASHINGTON, February 10, 1934.

[28] W. V. Mayneord, Brit. Jour. Radiology, N.S. vol. 6, p. 321, 1933.

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THERMAL EXPANSIONS OF SOME SODA-LIME-SILICA GLASSES AS FUNCTIONS OF THE COMPOSITION

By B. C. Schmid, A. N. Finn, and J. C. Young

ABSTRACT

The linear thermal expansions from 25 C to the "critical" and "softening" temperatures were determined for 19 soda-silica and 30 soda-lime-silica glasses by the interferometer method. Graphs have been prepared from which the critical termperature, softening temperature, the expansions to these temperatures, and the annealing range can be predicted approximately for any glass in the range of compositions studied.

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I. INTRODUCTION

This report is the third of a series of studies on the relation between chemical composition and properties of some soda-lime-silica glasses. In the first report, relating to index of refraction,[1] the purpose of the general study was given, the method of making the glasses was detailed, essential parts of the methods of chemical analyses were outlined, and the character of annealing was described. The second report contained the results obtained with respect to density,[2] and the present paper gives the results obtained by measuring the thermal expansion of 37 of the glasses used in the previous studies and 12 additional glasses made especially for the current study. Of the total number 19 were soda-silica and 30 were soda-lime-silica glasses, the composition varying so that the former contained approximately from 17 to 50 percent soda and the latter from 3 to 20 percent lime.

The linear thermal expansion of each glass from 25 to 400 C, to the critical temperature, and to the softening temperature, and also these critical and softening temperatures are included in the data presented.

[1] Faick, C. A., and Finn, A. N., The index of refraction of some soda-lime-silica glasses as a function of the composition, B.S. Jour. Research, vol. 6 (RP320), p. 993, June 1931; also Jour. Am. Cer. Soc., vol. 14, no. 7, p. 518, 1931.

[2] Glaze, F. W., Young, J. C., and Finn, A. N., The density of some soda-lime-silica glasses as a function of the composition, B.S. Jour. Research, vol. 9 (RP507), p. 799, Dec. 1932.

II. METHOD USED

Expansion measurements were made by the interferometer method described by Peters and Cragoe,[3] which consists essentially of placing three small truncated cones of glass about 5 mm high between two optically flat fused-quartz disks and counting the number of interference fringes which pass a reference point in the viewing apparatus as the temperature of the furnace is raised at a rate of approximately 3° C per minute.

Expansion measurements were made in duplicate on all the soda-lime-silica glasses, and the second measurements were regarded as the more satisfactory because such measurements were, in general, more nearly reproducible than those obtained in the first test. In all cases of duplication the data reported are from the second test. Because of the unstable (hygroscopic) nature of most of the soda-silica glasses and the consequent difficulty in handling them, their expansions were in many cases measured only once and the data, except for a few of the more stable glasses, are based on single tests.

III. DATA OBTAINED AND RESULTS

The composition of each glass, the expansion from 25 to 400 C, the critical temperature, the expansion from 25 C to the critical temperature, the softening temperature, and the corresponding expansion are given in table 1. The viscous deformability of a glass increases rapidly between the so-called critical and softening temperatures. At the critical temperature the rate of deformation is too low to result in measurable deformations under the conditions of operation in these expansion tests; as the softening temperature is approached, however, the rate of deformation becomes so great that it results in a fairly rapid and measurable flattening of the bearing points of the test specimen under the weight of the interferometer plate. When determined under the same experimental conditions, these temperatures are rather characteristic of a given glass and it is presumed also that under such conditions they give a fairly good method of showing at what temperatures different glasses reach comparable deformabilities.

The critical temperature, or the temperature at which the rate of expansion definitely increases, was regarded as the temperature at which a straight line drawn through four or five consecutive points on the expansion-temperature curve departed definitely from a line drawn through the next higher points.

The softening temperature for any glass was relatively easily determined because, for the purpose of this paper, it was regarded as the temperature at which the glass became so soft that its rate of shortening by deformation was equal to its rate of expansion and the movement of the interference fringes practically ceased. This point was followed by a reversal in the direction of movement of the fringes, caused by increasing deformation of the specimens.

Since the temperature at which expansion measurements were started varied between 25 and 39 C, all expansions were "corrected" to 25 C as a starting point. This extrapolation was made on the assumption that the rate of expansion between 100 and 200 C is

[3] B.S. Scientific Papers, vol. 16 (S393), p. 449, 1920. See also Merritt, G. E., B.S. Jour. Research, vol. 10 (RP515), p. 59, 1933.

TABLE 1.—*Compositions, observed critical and softening temperatures, and linear thermal expansions between the indicated temperatures*

Glass number [1]	Composition [2]			Expansion [3] (25 to 400 C)	Critical temperature [3]	Expansion [3] (25 C to critical temperature)	Softening temperature [3]	Expansion [3] (25 C to softening temperature)
	SiO_2	Na_2O	CaO					
	Percent	*Percent*	*Percent*	*Microns per cm*	°C	*Microns per cm*	°C	*Microns per cm*
1 (3)	52.15	47.85	----------	81 (+2)	----------	----------	440 (0)	95 (+2)
2 (6)	54.14	45.86	----------	76 (0)	426 (+2)	84 (−1)	450 (+3)	94 (+1)
3 (8)	57.45	42.55	----------	73 (+2)	428 (−5)	81 (−1)	460 (+3)	89 (−1)
4 (12)	59.97	40.03	----------	70 (+2)	442 (+2)	80 (0)	460 (−5)	85 (−2)
5 (14)	62.86	37.14	----------	66 (+2)	445 (−2)	76 (0)	470 (−4)	82 (−2)
6 (16)	65.30	34.70	----------	61 (+1)	457 (+4)	73 (0)	490 (+7)	80 (−1)
7 (19)	67.14	32.86	----------	58 (0)	460 (+2)	69 (−2)	490 (+2)	77 (−2)
8 (20)	69.65	30.35	----------	55 (+2)	470 (+5)	67 (0)	505 (+9)	76 (0)
9 (21)	70.21	29.79	----------	55 (+2)	470 (+3)	68 (+2)	500 (+2)	76 (+1)
10 (22)	70.44	29.56	----------	55 (+3)	467 (0)	68 (+2)	500 (+1)	77 (+2)
11 (23)	72.15	27.85	----------	51 (0)	473 (+2)	64 (0)	500 (−4)	72 (0)
12 (28)	76.60	23.40	----------	44 (+1)	480 (−3)	56 (0)	510 (−8)	63 (−1)
13 (29)	76.65	23.35	----------	44 (+1)	485 (+2)	58 (0)	510 (−8)	65 (0)
14 (31)	77.85	22.15	----------	41 (0)	486 (−1)	53 (−1)	525 (+3)	63 (0)
15 (32)	78.61	21.39	----------	40 (0)	490 (+2)	53 (0)	520 (−4)	60 (−1)
16 (33)	79.73	20.27	----------	38 (0)	489 (−1)	50 (−1)	530 (+2)	57 (−2)
17	80.04	19.96	----------	38 (0)	492 (+5)	50 (0)	525 (−4)	55 (−3)
18	82.72	17.28	----------	34 (0)	495 (−5)	45 (0)	540 (+2)	53 (0)
19 (34)	82.76	17.24	----------	34 (0)	500 (0)	45 (0)	550 (+12)	52 (−1)
[4] 20 (38)	100	----------	----------	----------	1,020	5	1,140	6
21	52.20	27.97	19.83	59 (−1)	498 (−7)	80 (0)	535 (+3)	90 (0)
22 (41)	54.37	32.85	12.78	62 (−3)	477 (+1)	79 (−2)	505 (−3)	83 (−6)
23 (42)	56.20	34.00	9.80	67 (0)	470 (+1)	84 (+5)	495 (−6)	90 (+2)
24	56.34	23.91	19.75	51 (−1)	517 (−10)	73 (−3)	550 (−4)	80 (−6)
25 (43)	56.76	37.48	5.76	67 (0)	444 (−9)	77 (−4)	480 (−4)	87 (−3)
26 (44)	58.41	38.54	3.05	68 (+1)	437 (−9)	77 (−2)	473 (−3)	88 (−2)
27	60.05	19.79	20.16	49 (+1)	548 (−2)	74 (+3)	580 (+1)	81 (−1)
28 (45)	60.32	24.50	15.18	52 (0)	520 (+1)	74 (+1)	547 (−3)	79 (−3)
29	62.93	17.39	19.68	43 (−1)	568 (+3)	69 (0)	595 (−1)	77 (−1)
30 (46)	63.34	24.39	12.27	52 (+1)	518 (+5)	74 (+2)	550 (+2)	81 (0)
31 (47)	64.14	21.22	14.64	47 (0)	530 (−5)	69 (0)	570 (+1)	76 (−2)
32 (48)	64.70	26.84	8.46	52 (0)	493 (−2)	71 (+1)	530 (−2)	81 (+2)
33 (49)	65.71	28.79	5.50	53 (0)	493 (+12)	72 (+2)	515 (−1)	79 (0)
34	66.05	17.92	16.03	44 (+1)	563 (+6)	69 (+3)	595 (+5)	78 (+2)
35	66.12	13.97	19.91	40 (+2)	587 (0)	67 (+1)	625 (+3)	77 (+2)
36 (50)	66.47	21.74	11.79	48 (+2)	522 (−4)	72 (+6)	560 (−2)	84 (+8)
37	67.23	11.62	21.15	37 (+2)	601 (−2)	64 (−1)	645 (+1)	75 (0)
38 (51)	67.30	29.43	3.27	53 (0)	480 (+7)	69 (−1)	515 (+5)	78 (+1)
39 (52)	67.98	22.50	9.52	47 (0)	518 (+1)	68 (+2)	560 (+6)	82 (+7)
40	70.12	15.03	14.85	39 (+1)	567 (−9)	63 (+1)	610 (−1)	73 (+2)
41 (53)	70.50	23.00	6.50	45 (−1)	506 (0)	62 (−1)	545 (−1)	73 (0)
42	71.70	12.10	16.20	35 (+1)	598 (−2)	60 (0)	630 (−6)	65 (−3)
43 (54)	72.08	14.21	13.71	36 (0)	571 (−8)	59 (−1)	615 (0)	68 (−1)
44 (55)	72.61	24.24	3.15	46 (+1)	490 (−2)	61 (0)	530 (+1)	72 (+1)
45 (56)	74.09	15.23	10.68	36 (0)	555 (−8)	57 (−2)	600 (−1)	68 (+1)
46 (57)	74.69	12.28	13.03	33 (−1)	589 (−4)	57 (0)	627 (−4)	66 (−1)
47 (58)	75.48	15.26	9.26	36 (0)	553 (−5)	54 (−3)	600 (+3)	65 (0)
48	78.56	18.45	2.99	38 (+1)	504 (−7)	52 (−1)	545 (−8)	60 (0)
49 (59)	78.77	16.33	4.90	34 (−1)	523 (−8)	51 (−1)	565 (−9)	61 (+1)
50 (60)	80.59	16.17	3.24	32 (−2)	505 (−17)	43 (−6)	560 (−1)	55 (−4)

[1] Figures in parentheses in this column are the numbers of the corresponding glasses in the report cited in footnote 2 of the text. Additional glasses made for this study have only 1 number.

[2] The methods of analyses of these glasses are discussed in the reports cited in footnote 1 of the text.

[3] Figures in parentheses in these columns are the algebraic differences, to the nearest whole number, between the observed values and those obtained by computation or from the graphs in figures 1, 2, or 3; + differences indicate observed values greater than computed values.

[4] The data on fused quartz (not published) were furnished by G. E. Merritt and are the average from several samples which were neither made nor analyzed at this Bureau.

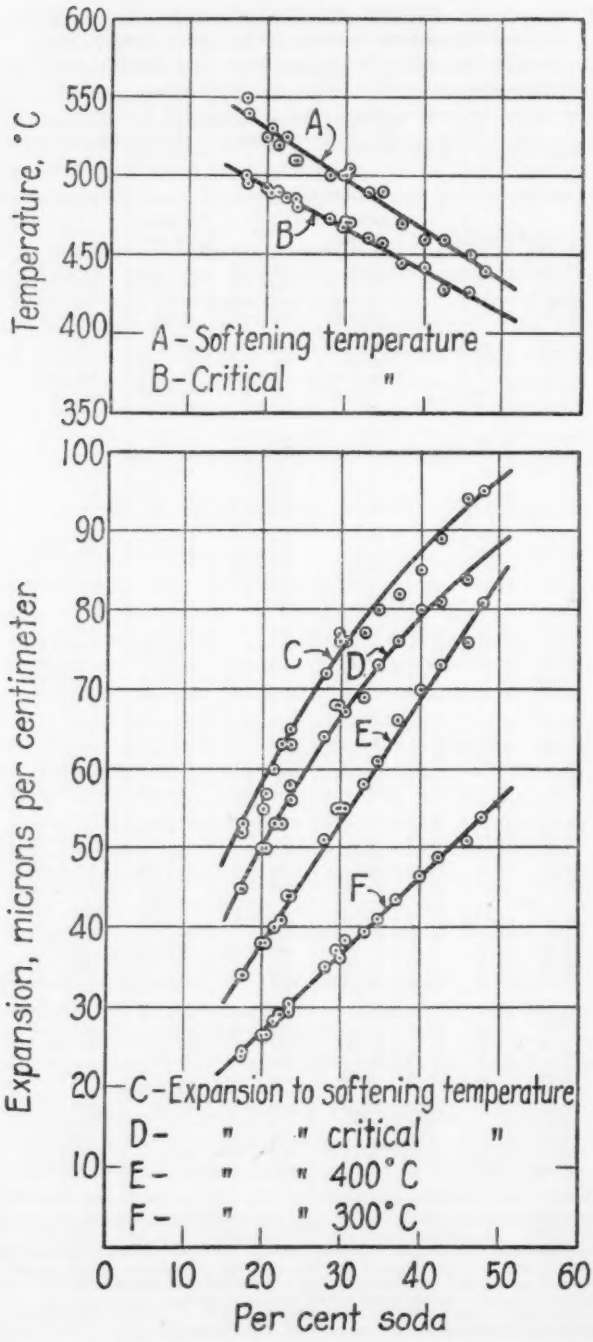

FIGURE 1.—*Diagram showing relations between composition, critical and softening temperatures, and linear expansions of some soda-silica glasses.*

practically constant and equal to the rate between 25 and 100 C. The maximum "correction" was 2 microns, the average being less than 1 micron.

The critical and softening temperatures of the soda-silica glasses and corresponding expansions (all obtained as described above) and also the expansions to 300 and 400 C are plotted in figure 1 against the soda content.

If the expansions from 25 C to any specific temperature, T, below the approximate critical temperature are considered, it was found that these expansions can be computed from equations of the familiar form $E=aA+bB+cC$, in which E is the linear expansion in microns per centimeter; A, B, and C are the percentages of silica, soda, and lime, respectively, and a, b, and c are constants determined for a given temperature. The values of these constants for each interval 25 C to T as T was increased by 50 C steps from 50 to 450 C were determined by making independent solutions by the method of least squares, and by using the expansion values of the various glasses as read from the individual expansion curves corrected to 25 C. The soda-silica and soda-lime-silica glasses were treated separately. In this way it was found that a, b, and c are functions of temperature, fitting very closely the equations:

$$a=0.00036t-0.00000036t^2$$
$$b=0.00245t+0.0000046t^2$$
$$c=0.00116t+0.0000010t^2$$

where $t=T-25$ C. The coefficients of t and t^2 for a, b, and c, respectively, were obtained by the method of least squares, using the various values of a, b, and c, determined as indicated above, for the different temperature intervals. The numerical values shown are those obtained from the soda-lime-silica glasses only. Although a solution of the soda-silica glasses gave only slightly different equations for a and b, less weight should be attached to them because, as previously stated, they are based on the first determinations (second determinations being used for the lime-glass data). For the purpose of evaluating the constants, no temperature above 450 C was used, since many of the glasses are approaching their critical temperatures at this point, and hence any solution involving data above 450 C would be of doubtful value. The equations were found, however, to be adequate within about 50 C of the critical temperature for any glass, a few such temperatures being as high as 600 C. The average deviation increases with temperature, being about 0.3 micron at 50 C and about 1.5 microns at 550 C, (the corresponding maximum deviations being 1 and 3 microns respectively) and at no temperature is there a noticeable systematic deviation, as long as no glass is considered after it comes within 50 C of its critical temperature.

Graphs E and F in figure 1 show observed linear expansions of the soda-silica glasses at 300 and 400 C, and also the lines obtained by solving the equations given above for E, a, and b being evaluated at these temperatures.

Based on the data obtained, several different kinds of empirical equations for computing the critical and softening temperatures and the expansions from 25 C to these temperatures for a given glass in either series can be devised. The following empirical relations were used, however, to compute the residuals presented along with the last

four columns in table 1. For both the critical and softening temperatures

$$T=d+e(B+C)+p\left(\frac{C}{B}\right)+q\left(\frac{C}{B}\right)^2$$

For the expansion to both temperatures

$$E=f+gB+hB^2+r\left(\frac{C}{B}\right)^n$$

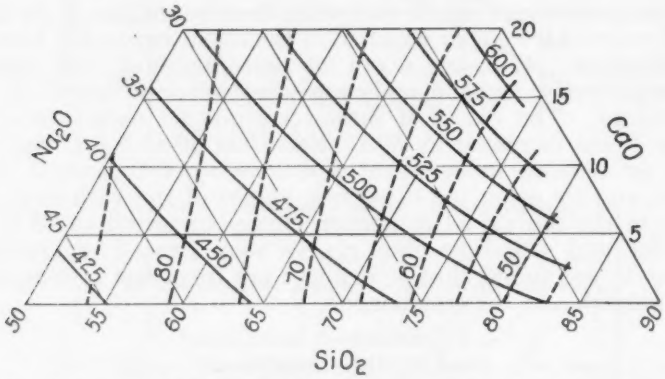

FIGURE 2.—*Diagram showing relations between composition of some soda-lime-silica glasses and critical temperatures (solid lines) and also linear expansions (broken lines) to those temperatures. Temperatures are given in C and expansions in microns per cm.*

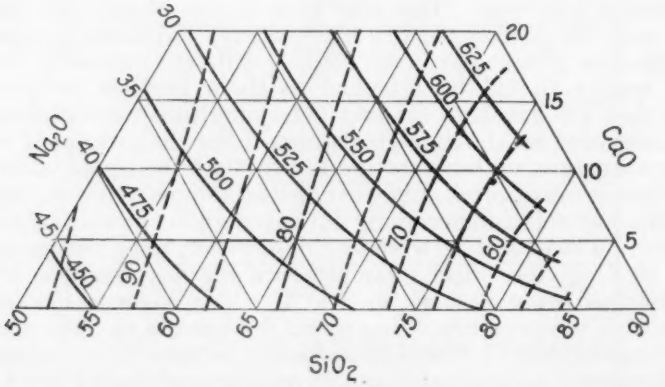

FIGURE 3.—*Diagram showing relations between composition of some soda-lime-silica glasses and softening temperatures (solid lines) and also linear expansions (broken lines) to those temperatures. Temperatures are given in C and expansions in microns per cm.*

In these equations B and C are the percentages of soda and lime, respectively, and d, e, f, g, h, p, q, r, and n are constants having somewhat different values in computing the data relating to the critical and softening temperatures. For example, p, q, f, and r remain practically unchanged, while h, the coefficient of B^2, changes approximately 30 percent. Actual use of numerical values for these constants was not made, however, since a graphic method based on the above relations

was found to be both simpler and adequate for determining both the differences (see table) and the lines (see figs. 2 and 3), which show how the composition of these glasses may vary without changing one of the following: The critical temperature, the softening temperature,[4] or the expansion to one of these.

IV. REPRODUCIBILITY AND ACCURACY OF RESULTS

Generally any one glass gave reproducible expansion measurements within 1 or 2 microns and temperature measurements within 5 degrees if the same specimens were used for a second series of measurements. The average difference between duplicate measurements of the expansions to the softening points, of the 34 glasses on which two tests were made, was 2 microns; measurements on 23 of the glasses varied 2 microns or less, on 5 glasses the difference was 3 microns and on the remaining 6 the average was 6, the maximum being 8 microns.

To demonstrate the effect of the shape of the sample on these results, two sets of specimens were prepared. For one of these the truncated cones were very stocky, that is they were relatively broad at the base, with only a slight taper and relatively flat, though rounded, at the top. For the other, the specimens had a smaller base and the cone was reduced to the equivalent of a very slender rod with a rather sharp point at the top. As might be expected, the critical temperature and expansion to that temperature were not significantly affected by shape, but the softening temperature and expansion of the slender specimen were 595 C and 79 microns, while similar values for the stocky specimen were 610 C and 91 microns, respectively. Hence under these conditions it is evident that one might obtain a difference of 15 C in softening temperature and 12 microns in expansion, depending upon the shape of the specimens used. No such extreme differences in shape existed between the specimens used in determining the data presented in table 1, but there were certainly some differences and these would account to some extent for such irregularities as occur in the softening temperatures and corresponding expansions. As a matter of fact, the unavoidable differences in shape of the points of the specimen which are in contact with the interferometer plates have ordinarily more significance than the shape of the body of the specimen and it is probably the relatively rapid flattening of these points during the first test which causes a portion of the differences between first and second tests.

Comparison of the data on the soda-silica glasses reported in this paper with that of Turner and Winks [5] shows certain differences. For instance, their data on any one glass plot as a comparatively straight line up to the critical temperature, while the expansion values obtained at different temperatures in the present work plot more definitely concave upward. Also, their expansions for the lower temperature ranges are somewhat (approximately 2 microns) higher, although their softening temperatures (called annealing temperatures, A_t) and the expansions to these temperatures are somewhat lower than those obtained in the present case. Their softening temperatures, for example, conform reasonably well to a straight line

[4] For practical purposes, and also within the limits of accuracy of the data, it can be stated that the critical temperatures are approximately 93.5 percent of the softening temperatures and that the expansions to the critical temperatures are approximately 88.5 percent of the expansions to the softening temperatures. However, different conditions of annealing may materially change the latter figure.

[5] Jour. Soc. Glass Tech., vol. 14, p. 110, 1930.

about 7° C lower than curve A in figure 1. Their temperatures, designated by "C_t," are also lower than the critical temperatures reported in this paper and do not agree with them except in a general way.

These differences are not surprising when one considers that the data were obtained by two distinctly different methods of measurement which involved the use of specimens of decidedly different length (5 mm as compared with 100 mm used by Turner and Winks); also, differences in the size of furnaces used and the consequent difficulty of obtaining uniform and reproducible temperature distribution should not be overlooked. It is thought that expansion measurements made by the interferometer method are very satisfactory for obtaining comparative data, because small samples can be used and also because no standard material of known thermal expansion is necessary for calibrating the apparatus.

V. ANNEALING RANGE

The proper annealing of glass is a problem which confronts every glass manufacturer and much has been written on the subject. The most noteworthy contribution is that by Adams and Williamson,[6] who point out the desirability of using different annealing temperatures for the same kind of glass, the actual temperatures used being dependent on the thickness of the piece to be annealed.

The annealing range for most commercial glassware lies between the critical and softening temperatures, but since the time required for annealing increases as the annealing temperature decreases, the optimum annealing temperature for any given piece will be as close to the softening temperature of the glass from which it is made as is consistent with the cooling rate that will be obtained in the lehr. Since the critical and softening temperatures of glasses of the soda-lime series may be read from figures 2 and 3, the approximate temperature ranges in which such glasses can be annealed may be readily estimated, but in this work no consideration has been given to the time required for annealing at various temperatures in the annealing range.[7]

VI. SUMMARY

The data and graphs in this paper, based on 19 soda-silica and 30 soda-lime-silica glasses, show the changes in thermal expansion, critical temperature, softening temperature, and annealing range of soda-lime-silica glasses with changes in composition in the range between approximately 12 and 50 percent soda, 0 and 20 percent lime, and 50 and 80 percent silica.

WASHINGTON, January 17, 1934.

[6] Jour. Frank. Institute, vol. 190, pp. 597–631 and 835–870, 1920.

[7] For information on time-temperature annealing effects and schedules, see reference cited in footnote 6. See also Tool, A. Q., and Valasek, J., B.S. Scientific Paper 358, 1919; and Finn, A. N., Jour. Am. Cer. Soc., vol. 9, no. 8, p. 493, 1926.

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APPARATUS FOR MEASURING THERMAL CONDUCTIVITY OF METALS UP TO 600 C

By M. S. Van Dusen and S. M. Shelton

ABSTRACT

Apparatus for measuring the thermal conductivity of metals up to 600 C is described. The method employed consists in comparing the conductivity of a metal, either directly or indirectly, with that of lead. Lead was selected as the standard since previous measurements have established its conductivity within fairly close limits. Determinations are made by measuring the axial temperature gradients in two cylindrical bars soldered together end to end, one end of the system being heated and the other cooled, and the convex surfaces protected from heat loss by a surrounding guard tube. Data are given on the conductivity of commercial nickel, high purity zinc, high purity nickel, and several commercial nickel-chromium and other alloys widely used for heating elements and thermocouples.

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I. INTRODUCTION

The thermal conductivity of metals is of considerable theoretical and practical interest, and numerous publications on the subject have been made. Perhaps for no other definite thermal property are the published results so widely divergent and subject to such great uncertainty, particularly at high temperatures. This may be attributed in part to the inherent difficulties of measurement, but perhaps to an even greater extent to the fact that the conductivity of a metal or alloy is sensitive to heat treatment, crystal structure, and slight changes in composition. In fact the exact description of a polycrystalline specimen, necessary and sufficient for its reproducibility so far as conductivity is concerned, is in many cases about as uncertain as the value of the conductivity itself.

The Bureau of Standards has received numerous requests for determinations of the thermal conductivity of particular metals, primarily alloys for special industrial purposes, and it therefore seemed desirable to set up an apparatus with which such tests could be made from time to time, over a considerable range of temperature.

The great sensitivity of thermal conductivity to changes in composition of alloys, and to the physical condition of the constituents, suggests the possibility that such measurements may in some cases be useful in metallographic investigations.

II. METHOD OF MEASUREMENT

Methods used for determining the thermal conductivities of metals have varied widely, both steady heat flow and variable heat flow having been employed. In nearly all cases "absolute" determinations have been made, which involve measurements of quantities of heat. The comparative method of using two specimens, one of known conductivity, through which heat flows in series, appeared to offer great simplification and to be less subject to uncertainty, particularly at high temperatures. This method, which seems first to have been employed by Berget,[1] has been used in the present work.

In the measurements to be described lead was selected as the primary standard, since it appeared to be the most suitable for the purpose, and previous measurements had established its conductivity at ordinary temperature within fairly close limits. If it eventually proves necessary or desirable, it will be possible to determine the absolute conductivity of the lead actually used, under conditions most favorable to accuracy. Such a determination need be made at but one mean temperature. On account of the undesirable mechanical properties of lead, a specimen of nickel previously compared with lead was used as the working or secondary standard in routine measurements.

The method employed consists in measuring the axial temperature gradients in two cylindrical bars soldered together end to end, one end of the system being heated and the other cooled, and the convex surfaces protected from heat loss by a surrounding guard tube. When a steady state has been attained, the heat flux is the same in both bars, and the conductivity at any point in either bar is inversely proportional to the temperature gradient at that point. If the absolute value of the conductivity of the metal of one bar is known at some temperature within the experimental range, that of the metal of the other bar can be calculated at all points at which the gradient has been measured. Gradients cannot be directly observed, but can be calculated from direct measurements of temperature distribution along the bars. By using the same procedure and employing a bar of a single material, the temperature coefficient of conductivity of the material of this bar can be determined without reference to other materials.

III. DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

Elaborate refinement of apparatus to obtain great precision was not attempted. Such refinements did not appear to be warranted, at least for measurements on polycrystalline materials. The aim was to construct an apparatus of comparatively simple design, with which a precision of better than 2 percent might be expected.

A cross section of the apparatus with test specimens in place is shown in figure 1. The specimen to be measured (A), 15 cm long and 2 cm in diameter is soldered to the copper cylinder (C) which serves as a heat collector from the surrounding heating coil. The standard bar (B), 5 cm long and 2 cm in diameter, is soft soldered between specimen (A) and the brass chamber (J), through which water at constant temperature is circulated. Tin is ordinarily used

[1] Berget, Comp. Rend. 105, p. 224, 1887.

for joining the two bars, and low melting point solder (Bi–Sn eutectic) for attaching the water cell. Tin is also used to provide thermal contact between specimen (*A*) and the copper cylinder. At higher temperatures the thermal contact is not impaired, since the copper alloys with the tin and produces a hard soldered joint.

The copper cylinder (*C*), 8.5 cm long and 3 cm in diameter, is surrounded by a heating coil of chromel A ribbon wound on a thin-walled alundum tube (*G*), 8 cm long and 4 cm in outside diameter.

The guard or shield tube (*D*), made of chromium-nickel stainless steel (18–8), is 23 cm long, 6.8 cm outside diameter, and has a wall thickness of 0.8 cm. The top is jointed and soldered to a nickel tube (*E*) of the same cross section and 5 cm long. A copper tube (*K*), 0.4 cm inside diameter, through which constant temperature water circulates, is soldered around the top of the nickel tube. The shield tube is heated at its base by a heating unit consisting of 6.3 ohms of chromel ribbon wound around alundum tube (*H*), 8 cm long and 5.6 cm outside diameter.

The copper ring-shaped disk (*N*), 12 cm in outside diameter, is soldered to the shield tube at the joint between the steel portion and the nickel portion. Spiral grooves are cut on both sides of this ring and a heating unit consisting of no. 22 chromel wire insulated with glass beads is cemented into the grooves. This auxiliary heating unit is necessary for accurate control of the temperature of the guard tube. The portion of the guard tube above the ring heater is made of nickel, a much better heat conductor than chromium-nickel steel, in order that proper adjustment of the temperature of the guard would always be possible by supplying heat at the joint between nickel and steel. If the guard tube consisted of the same metal throughout its length, it would be necessary in some cases to cool the region where the ring heater is located, a procedure which was considered less convenient than making the guard tube in two sections.

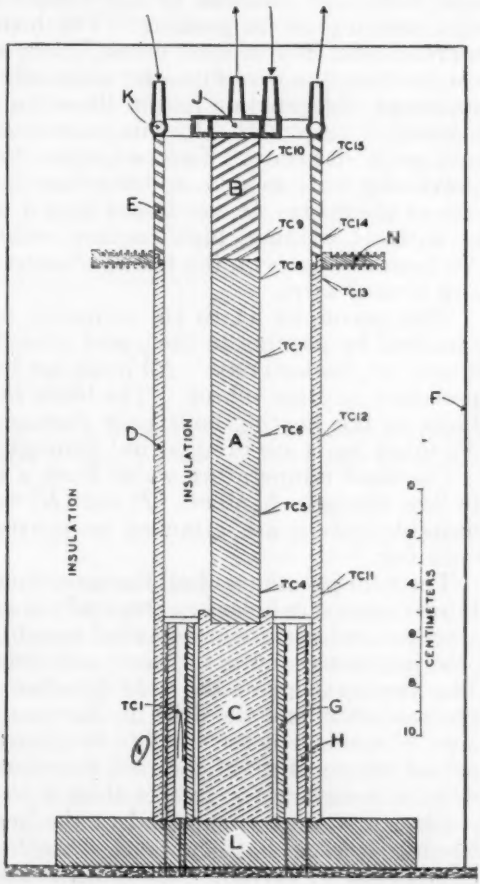

FIGURE 1.—*Cross section diagram of apparatus.*

The guard tube, heating coils, and copper cylinder rest on an alundum disk (*L*), 2.5 cm thick and 14 cm in diameter. The appa-

ratus and alundum base are surrounded by a galvanized steel case (*F*), about 20 cm in diameter, split longitudinally into two halves for convenience. The entire assembly rests on asbestos board and is insulated underneath with insulating brick. The annular spaces between the test specimens and guard tube, and between the latter and the steel case, are filled with diatomaceous earth for thermal insulation.

Thermocouple 1 is placed between the heating coils (*G*) and (*H*) to facilitate temperature control. Thermocouples 4 to 10, inclusive, used for measurement of temperature distribution along the test specimens, are attached to the surface of the bar either by electric spot welding or by peening. The latter method was found to be more satisfactory in most cases. Very small transverse cuts slightly deeper than the wire diameter are made on the convex surface of the specimen, the junction laid in the cut and peened in by tapping with a hammer or punch. In this process the cut closes up on the wire and grips it firmly. The two wires forming the thermocouple are previously butt welded, and the junction reduced to about the same size as the wire. It was found that if the wires were merely peened in without welding, high contact resistances sometimes developed. All thermocouples on the test specimens are made of no. 36 chromel P and alumel wires.

Thermocouples 11 to 15, inclusive, of no. 22 chromel-alumel, are attached by peening to the guard tube directly opposite couples 6, 8, 9, and 10, respectively. All leads are insulated with short lengths of porcelain or glass tubing. The leads to thermocouple 1 and connections to the heating coils pass through the base of the apparatus. All other leads are brought out through the open top.

Constant temperature water from a thermostated tank is allowed to flow through chambers (*J*) and (*K*) through separate rubber tubes. Suitable valves are attached to control the rates of flow in each chamber.

The cold junctions of all thermocouples are contained in small glass tubes inserted in holes in a thermally insulated aluminum block. This arrangement assures substantial equality in the temperatures of the cold junctions, and is far more convenient than the use of ice baths. The temperature of the cold junction is observed with a mercury thermometer, and the drift in this temperature during the course of a set of readings is too small to be of any significance whatever. The actual temperature of the cold junction is of course easily measured with an accuracy far greater than is required.

Electric energy is supplied to the heating coils (*G*) and (*H*) by a 60-volt storage battery, and suitable rheostats are provided for adjustment of current. The disk heater (*N*) is supplied with alternating current from the switchboard, since constancy of power supply to this coil is not vital. In making an experiment, the system is heated up rapidly with ac to the desired temperature and then switched over to dc. Currents in the individual heating elements are then manually adjusted from time to time until an approximately steady state is attained and the temperatures at corresponding points on specimens and guard tube are approximately equal. This procedure requires several hours on account of the considerable quantity of lagging around the apparatus. At the time thermocouple readings are made, a certain amount of drift in the temperature of the hot end can be tolerated without significant error. This point as well as the

question of required degree of equality of temperatures of tube and specimen will be discussed in a later section. To eliminate the effect of drift, thermocouple readings are taken at equal intervals of time (usually one half minute), beginning at the hot end, proceeding to the cold end, and repeating readings back to the hot end. The averages of the two readings at each point give a set of readings substantially the same as would be obtained if all thermocouples could be observed simultaneously. Several such sets of readings are ordinarily made in the course of a day.

The temperature distribution along the specimen (or specimens) is calculated from the thermocouple readings and the measured positions of the junctions along the bar. The temperature gradient at the mean temperature between two adjacent junctions is taken as the ratio of the temperature difference between the junctions and the distance between them. No appreciable error is introduced by taking finite differences, since the temperature as a function of distance along the specimen has in all cases only a small curvature. If a value for conductivity is assigned for some temperature within the experimental range, values at other temperatures can be calculated by the relation:

$$K\frac{dT}{dx} = K\frac{\Delta T}{\Delta x} = \text{constant}$$

where K = thermal conductivity

and $\frac{dT}{dx} = \frac{\Delta T}{\Delta x}$ = temperature gradient.

This relation obviously holds for a bar consisting of two specimens of the same diameter placed end to end, as well as for a specimen of a single material.

IV. TESTS TO DETERMINE PRECISION OF METHOD

To determine the precision of measurement attainable in the type of apparatus described, a series of experiments on three metallic specimens was made. In addition to lead, the primary standard, nickel and zinc were selected for this purpose. These metals will be designated as reference standards. The general plan was to intercompare these metals in all possible combinations and observe the consistency of the results obtained.

Determination of the temperature coefficients of thermal conductivity of the three metals was first made. This was accomplished as already noted by placing the same metal in the A and B positions (refer to fig. 1). A number of experiments of this kind were made on each metal, using various temperature gradients in each case. Comparisons of the three metals were then made by placing the various materials in a number of combinations of the A and B positions. All the results obtained were calculated relative to lead, the thermal conductivity of which was assumed to be 0.352 watts cm^{-1} deg^{-1} at 0 C (Int. Crit. Tables, vol. 5, p. 182).

A typical example of a single set of readings is given in table 1. Readings of the thermocouples on the guard tube were taken at approximately the same time as those on the specimen, but the exact time is not significant, since the drift in temperature difference between tube and specimen is negligible over a considerable period.

TABLE 1.—*Typical example of set of thermocouple readings*

TC no.	Thermocouples on specimen			Emf	Thermocouples on tube	
	Time	Emf	Time		TC no.	Emf
	min	*μv*	*min*	*μv*		*μv*
4	0.5	10,308	6.5	10,315	11	10,190
5	1.0	8,422	6.0	8,426		
6	1.5	6,572	5.5	6,574	12	6,500
7	2.0	4,829	5.0	4,830		
8	2.5	3,132	4.5	3,132	13	3,037
9	3.0	2,256	4.0	2,256	14	2,147
10	3.5	585			15	571

A skeleton table of calculations for a lead specimen is given in table 2. The quantity $\Delta x/\Delta T$, the reciprocal of the temperature gradient, is proportional to the thermal conductivity. The numbers in the last column were obtained by assigning the value 0.352 watts cm^{-1} deg^{-1} to the value of the conductivity at 0 C. This process required a slight extrapolation since the lowest mean temperature at which the gradient was observed was 58 C.

TABLE 2.—*Skeleton table of calculations*

Thermocouple	Mean	Temperature	Temperature difference between specimen and shield tube	Mean temperature between adjacent thermocouples	Difference in temperature between adjacent thermocouples ΔT	Distance between adjacent thermocouples ΔX	$\frac{\Delta X}{\Delta T}$	Thermal conductivity watts cm^{-1} deg^{-1}
	μv	*°C*	*°C*	*°C*	*°C*	*cm*		
TC_4	10312	277.3	3.0	254	45.7	3.14	687 (x10⁻⁴)	0.305
TC_5	8424	231.6		209	45.1	3.14	697	.310
TC_6	6573	186.5	1.8	165	43.5	3.14	722	.322
TC_7	4830	143.0		122	42.7	3.15	738	.328
TC_8	3132	100.3	2.3					
TC_9	2256	78.6	2.7	58	41.3	3.16	765	.340
TC_{10}	585	37.3	0.3					

V. EXPERIMENTAL RESULTS

Description of the three metals, nickel, lead and zinc, used in the experiments described in the previous section is given in table 3. Results of all measurements on these metals are graphically represented in figures 2, 3, and 4. It will be noted that the results obtained with all combinations of the metals in the *A* and *B* positions are mutually consistent within about 2 percent. The conductivity of zinc as a function of temperature shows a slight but distinct curvature. Those of the other metals do not, but the curve for nickel shows a very abrupt change in direction at about the temperature of the magnetic transformation point.

Measurements have been made on a number of commercial iron alloys, the results of which are given in the following paper (RP669). In the present paper are included data on the thermal conductivity of nickel of high purity, as well as nickel-chromium and other alloys widely used for heating elements and thermocouples. These materials are described in table 4, and the results of conductivity measure-

ments are shown graphically in figures 5 and 6. Results on all materials described in this paper, interpolated from the experimental data, are given in table 5.

TABLE 3.—*Description of reference standards*

Designation	Material	Impurities	Description
(N.S.)	Nickel	Cu 0.14, Mn 0.09, Fe 0.60	Commercial malleable nickel. Specimen machined from hot rolled rod.
(L.S.)	Lead	Unanalyzed	Bureau of Standards melting point standard lead. Probably the purest lead available in usable quantity. Sample was cast in a bottom feed cast-iron mold and machined to proper dimensions.
(Z.S.)	Zinc	Pb 0.04, Fe 0.02 Cd, not detected	"Chemically pure" zinc. Sample cast in graphite mold and machined.

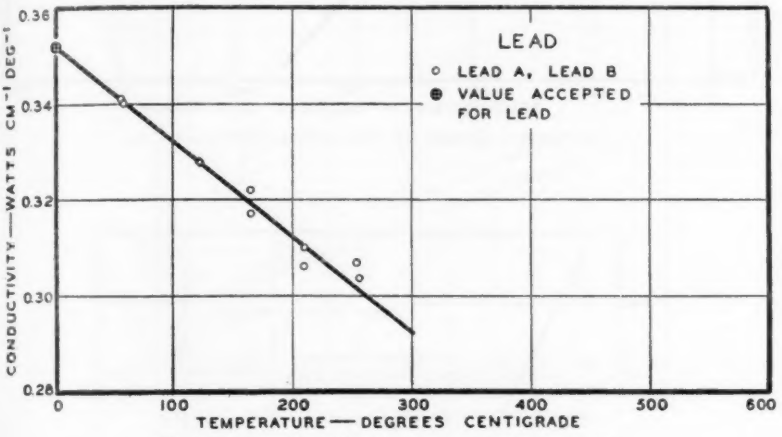

FIGURE 2.—*Results of measurements on lead.*

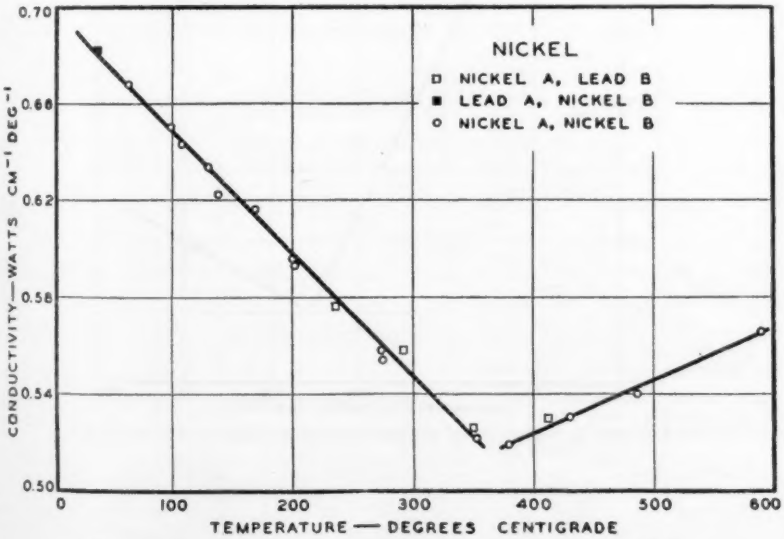

FIGURE 3.—*Results of measurements on commercial nickel.*

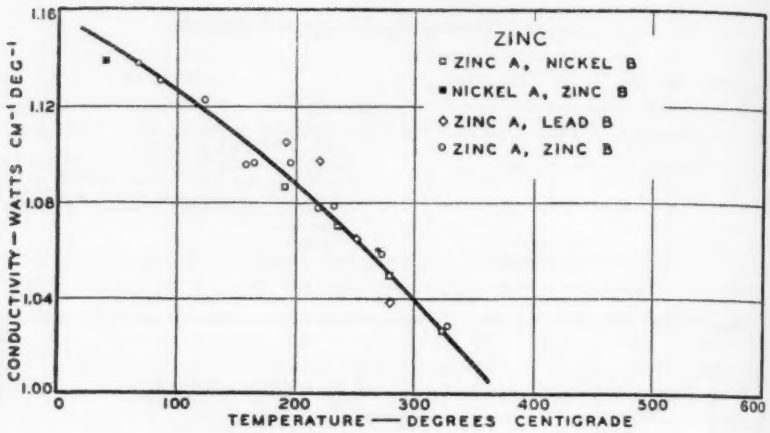

FIGURE 4.—*Results of measurements on zinc.*

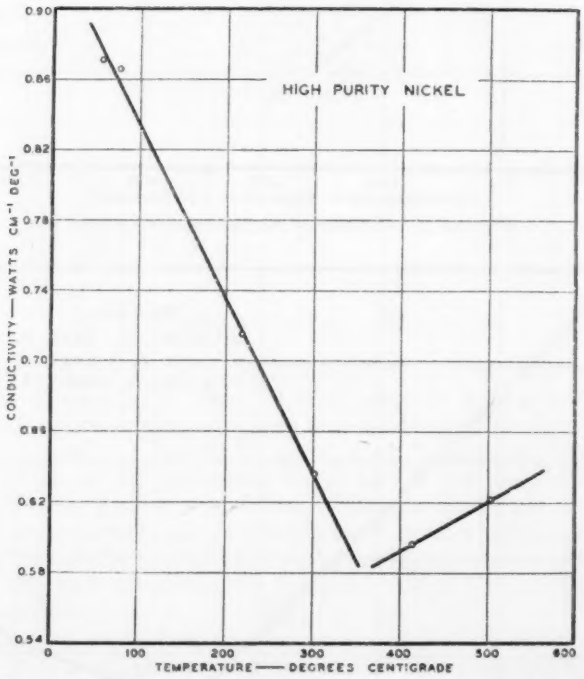

FIGURE 5.—*Results of measurements on high purity nickel.*

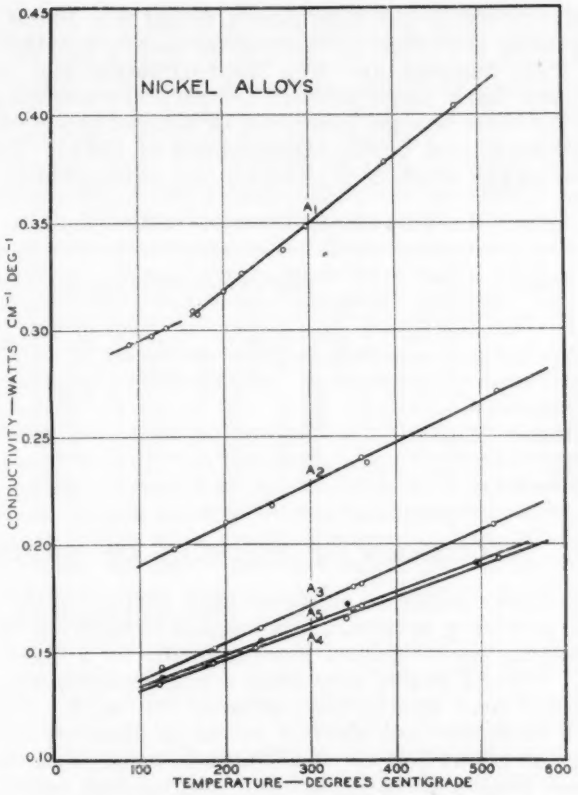

FIGURE 6.—*Results of measurements on alloys.*

TABLE 4.—*Description of test specimens*

Designation	Material	Chemical composition	Remarks
(N_1)	"High purity nickel."	Ni 99.94, C .005, S .004, Co .016, Si .006, Fe .03, Cu .006.	Melted in vacuum furnace and furnace cooled. Large crystals. Bureau analysis.
(A_1)	"Alumel"	Ni 95%, Al 2%, Mn 2%, Si 1%.	Pouring temperature 1,540 C. Cast in 5-in. diam. ingot. Hot rolled to 1⅝-in. sq bar. Tested in "as rolled" condition. Mfgrs. analysis.
(A_2)	"Chromel P"	Ni 90%, Cr 10%	Pouring temperature 1,540 C. Cast in 5-in. diam. ingot. Hot rolled to 1⅝-in. sq bar. Tested in "as rolled" condition. Mfgrs. analysis.
(A_3)	"Chromel A"	Ni 80%, Cr 20%	Pouring temperature 1,540 C. Cast in 5-in. diam. ingot. Hot rolled to ¾-in. round bar. Tested in "as rolled" condition. Mfgrs. analysis.
(A_4)	"Chromel C"	Ni 61%, Cr 16%, Fe 23%	Pouring temperature 1,540 C. Cast in 5-in. diam. ingot. Hot rolled to ¾-in. round bar. Tested in "as rolled" condition. Mfgrs. analysis.
(A_5)	"Chromel 502"	Ni 34%, Cr 10%, Fe 56%	Pouring temperature 1,540 C. Cast in 5-in. diam. ingot. Hot rolled to ¾-in. round bar. Tested in "as rolled" condition. Mfgrs. analysis.

The conductivity of the high purity nickel was found to be considerably greater than that of commercial nickel, but the percentage variation with temperature was approximately the same. The alloys all show fairly large positive temperature coefficients of conductivity, and there is some indication of a slight change in the slope of the curve for alumel in the neighborhood of 150 C. Since alumel is 95 percent nickel, an effect of this nature is quite possible.

TABLE 5.—*Interpolated results*

Designation	Metal	Thermal conductivity in watts cm^{-1} deg^{-1}						
		0 C	*100 C*	*200 C*	*300 C*	*400 C*	*500 C*	*600 C*
(L.S.)	Lead	0.352	0.332	0.312	0.292			
(Z.S.)	Zinc		1.123	1.085	1.048			
(N.S.)	Nickel		.649	.599	.549	0.524	0.546	0.569
(N_1)	High purity nickel		.828	.732	.638	.593	.621	
(A_1)	"Alumel"		.296	.318	.350	.381	.412	
(A_2)	"Chromel P"		.190	.209	.228	.247	.266	
(A_3)	"Chromel A"		.136	.154	.172	.189	.206	
(A_4)	"Chromel C"		.132	.147	.161	.175	.190	
(A_5)	"Chromel 502"		.134	.149	.163	.177	.192	

VI. DISCUSSION OF SOURCES OF ERROR

It was not practicable to calibrate each thermocouple separately, since it was necessary to attach new couples to each specimen tested, and the program contemplated measurements on a large number of specimens. Several lots of wire from a single source were annealed, calibrated, and used during the course of the work. Each lot was wound on a nichrome reel about 8 inches in diameter and annealed in a furnace at about 750 C. Calibrations made from time to time on specimens from a given lot showed insignificant variations. The duration and temperature of the several annealings were not exactly the same, and the calibrations of the various lots differed from each other by a few degrees at the higher temperatures. Even if a single calibration had been used for all the lots of wire which were separately annealed, the error in temperature differences would have been almost negligible, since the differences in emf at any given temperature are nearly proportional to temperature. An error of a few degrees in mean temperature would hardly be noticed, since the change in conductivity of metals with temperature is small. The magnitude of errors due to inhomogeneity of wires can only be judged by the precision of the results obtained. Such errors would not be systematic, and some of the scatter in the results can no doubt be attributed to this cause.

The effect of heat conduction to or from the junctions along the thermocouple wires was minimized by using fine wires of low conductivity metals, by attaching the junctions in good thermal contact with the metallic specimen, and by locating a portion (about 2 cm length) of the wires adjacent to the junction in a region having nearly the same temperature as the junction. The cuts into which the thermocouple wires were peened were made as small as possible, the continuity of the bar being but very slightly impaired by this process. Distances between junctions could be measured to 1 percent or better by means of a pair of dividers and a steel scale.

As a guide in the design of apparatus, a mathematical analysis of the effect of heat transfer between specimen and guard tube was made at the outset of the work. This calculation indicated that if a nickel specimen were maintained at temperatures 1° C different from those at corresponding points on the guard tube, the maximum error due to heat leakage would be only about 0.2 percent. With any given adjustment of temperatures, the error due to heat leakage is inversely proportional to the conductivity of the specimen, so that better temperature control is required in measuring relatively poor heat conductors than is the case with relatively good conductors. Experimental tests were made with a zinc specimen, and calculated results approximately verified. No great difficulty was experienced in regulating temperatures within a few degrees, and it is therefore believed that errors greater than 1 percent were rarely introduced by heat transfer between specimen and guard tube.

On account of the large amount of insulation surrounding the apparatus, a long time was required to approximate a steady state. It was therefore desirable to ascertain how great a drift in temperature could be tolerated without causing significant error. Calculation showed that for a nickel specimen a drift of about 0.1° C per minute at the hot end, when this was at 500 C, would introduce an error of only about 0.6 percent. A steady state within this limit can be attained in a few hours.

It was found experimentally that appreciable errors were introduced by imperfect soldered joints, the resulting distortion of the lines of heat flow affecting the temperature at the thermocouple junctions nearest the joints. The possible presence of an effect of this kind is shown up by a large drop in temperature across the soldered joint. When this is found, the joint requires resoldering. A few metals on which measurements have been made, e.g., chromium steels, are rather difficult to tin, but it has always been found possible to make joints having low thermal resistance.

VII. COMPARISON WITH PREVIOUS RESULTS

The values of thermal conductivity given in this paper depend upon the value assigned to lead. A critical review of the previous work on lead indicates that the value assumed is probably correct within about 3 percent. Most of the previous results are in fairly good agreement in the region of room temperature, but depart widely at both high and low temperatures. Temperature coefficients of conductivity range from practically zero to a 0.12 percent decrease per degree C, excluding some apparently unreliable data. The value obtained in the present work (which is independent of the absolute value assumed for the conductivity of lead) is 0.057 percent decrease per degree C. Of the more recent measurements extending above 0 C, Meissner [2] observed practically no change in conductivity between 0 and 100 C, King [3] found a decrease of 0.017 percent per degree between 90 and 210 C, Konno [4] a decrease of 0.037 percent per degree from 0 to 300 C, and finally, Bidwell and Lewis [5] observed

[2] Meissner, Ann. der Phys., vol. 47, p. 1001, 1915.
[3] King, Phys. Rev., vol. 11, p. 149, 1918.
[4] Konno, Sci. Rep. Tohoku Imp. Univ. ser. 1, vol. 8, p. 169, 1919.
[5] Bidwell and Lewis, Phys. Rev. vol. 33, p. 249, 1929.

a decrease of 0.12 percent per degree between −50 and 100 C. In the neighborhood of 0 C, all these experimenters report practically the same value for the conductivity itself.

Comparison of the present results on zinc with those obtained previously does not have much significance, since Bidwell and Lewis [6] have shown that the conductivity of high purity zinc is considerably affected by the method of preparation of the specimen. So far as the change in conductivity with temperature is concerned, the results reported here are in good agreement with those of Konno,[7] and in fair agreement with those of Schofield.[8] The conductivity values obtained by Konno are consistently 2.5 percent lower than those reported here, and those of Schofield average about 6 percent lower.

Previous results on nickel are widely divergent, probably on account of the relatively large effect of small amounts of impurities on the conductivity of this metal, as well as the difficulty in the past of securing material in a high state of purity. The only published results on the thermal conductivity of nickel comparable in purity with the N_1 (high purity) nickel measured in the course of the present work are those of Sager.[9] His values are in general higher than ours, although in the region of 100 C the agreement is good. At about 175 and 300 C, Sager's results are some 5 percent higher than ours, and at 400 and 550 C approximately 20 percent higher. Other results reported in the literature are much lower, roughly comparable with our results on the (N.S.) commercial nickel, although all show a less pronounced minimum.

The only thermal conductivity data on nickel-chromium alloys which have come to our attention are those of Smith,[10] who worked with a large number of binary alloys, including 90 Ni—10 Cr and 70 Ni—30 Cr. Measurements were made at one mean temperature, approximately 50 C. The value of 0.197 watt cm^{-1} deg^{-1} was obtained for the conductivity of 90 Ni—10 Cr alloy at 56 C, which can be compared with 0.18 watt cm^{-1} deg^{-1}, obtained in the present work for chromel P, nominally of the same composition. This agreement can be considered good, in view of the fact that the curve representing conductivity as a function of composition for this series of alloys is very steep at the 90 Ni—10 Cr composition. No measurements were made by Smith on 80 Ni—20 Cr alloy (essentially chromel A), but interpolation indicates that the agreement of his results with ours is probably considerably better at this point. Smith also made measurements at about 50 C on zinc and lead of high purity, obtaining results on both in agreement with ours within about 2 percent. He apparently made no measurements on nickel, although the nickel used in the preparation of the various alloys contained only about 0.2 percent of impurities excluding cobalt.

Acknowledgment is made to the Hoskins Co., who kindly furnished the nickel alloys used in the measurements described in this paper.

WASHINGTON, February 24, 1934.

[6] Loc. Cit. p. 439.
[7] Loc. Cit. p. 439.
[8] Schofield, Proc. Roy. Soc., London, series A, vol. 107, p. 206, 1925.
[9] Sager, Rensselaer Poly. Inst., Eng. and Science, series no. 27, 1930.
[10] Smith, Ohio State Univ. Eng. Exp. Stat. Bull. no. 31, 1925.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP669

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THERMAL CONDUCTIVITY OF SOME IRONS AND STEELS OVER THE TEMPERATURE RANGE 100 TO 500 C

By S. M. Shelton

ABSTRACT

The thermal conductivities over the temperature range 100 to 500 C have been determined for 20 irons and steels which were selected as typical examples of commercial materials used for a variety of purposes and expected to have considerably different thermal conductivities. The data on the chromium-iron anc chromium-nickel-iron alloys are of particular interest because of the lack of previous data on the thermal conductivity of "stainless" steels.

The apparatus was designed for comparative measurements and thus eliminated calorimetric or power-input determinations which are difficult to perform with uniformly high accuracy over a broad range of temperature. High-purity lead was used, either directly or indirectly, as the standard with which other metals were compared.

The results indicate that, in general, the differences in conductivity of irons and steels are much smaller at high temperatures than at room temperatures. High-alloy steels have lower thermal conductivities than low-alloy steels. The thermal conductivities of irons and low-alloy steels decrease with increase in temperature. The conductivities of the high-alloy steels increase with increase in temperature; in other words, an increase in the amount of alloying constituents in iron causes, in general, a decrease in thermal conductivity and an increase in the temperature coefficient. The many and sometimes conflicting factors concerned make it practically impossible to generalize on the quantitative relationship of thermal conductivity and total alloy content of ferrous metals.

A fairly complete bibliography of data on the thermal conductivity of iron and steel is given.

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I. INTRODUCTION

Previous determinations of the thermal conductivities of iron alloys are surprisingly few. Hall [1] gives an excellent summary of the investigations made by Forbes, Lorenz, Angstrom, Neumann and others during the nineteenth century. A fairly complete bibliography of subsequent data relating to the thermal conductivity of iron and its alloys is appended to this paper.

The primary object of most of the earlier researches was to correlate thermal and electrical conductivities. The test material was of secondary importance. Later tests were made on present day structural materials and the results are more reliable and have more practical application. Information on the thermal conductivity of

[1] E. H. Hall, concerning thermal conductivity of iron, Physical Review, vol. 10, p. 277, 1900.

structural materials over a range of temperature is of considerable importance within a limited field [2] in the selection of materials and in the design of structures.

In this paper are given results of the determination of the thermal conductivities of 20 miscellaneous irons and steels which were selected as typical examples of commercial materials used for a variety of purposes and were expected to have considerably different thermal conductivities. The data on the chromium-iron and chromium-nickel-iron alloys are of particular interest because of the lack of previous data on the thermal conductivity of stainless steels.

II. TEST METHOD

The method and apparatus used in the determinations given in this paper are described in detail in a separate paper.[3]

The apparatus was designed for comparative measurements and thus eliminated calorimetric or power-input determinations which are difficult to perform with uniformly high accuracy over a broad range of temperature. High-purity lead was used, either directly or indirectly, as the "standard" with which other metals were compared. The thermal conductivity of lead at ordinary temperatures is believed to be known with as high an accuracy as that of any metal.

The method consisted essentially in measuring the axial temperature gradients in two cylindrical bars, soldered together end to end. One end of the system was heated, and the other was cooled. The convex surface of the bars was protected from loss or gain of heat by a shield tube. After a steady state of heat flow has been attained, the heat flux is the same in both bars, and the conductivity at any point in either bar is inversely proportional to the temperature gradient at that point. If the absolute value of the conductivity of the metal of one bar is known at some temperature within the experimental range, the conductivity of the other metal can be calculated at all points where the temperature gradient has been measured.

III. MATERIALS AND RESULTS

The materials on which determinations were made are described in table 1.

The results of thermal conductivity determinations of the irons and low-alloy steels are shown graphically in figure 1. The results on the high-alloy steels, including chromium steels and a high-manganese nickel steel, are shown in figure 2, and those on the "eighteen-eight" type chromium-nickel steels in figure 3. Thermal conductivity values for different temperatures, interpolated from the experimental results, are listed in table 2. The value for the thermal conductivity of lead, 0.352 watts cm^{-1} deg^{-1} at 0 C (International Critical Tables, vol. 5, page 218) was used as the basis for all determinations.

[2] M. S. Van Dusen, note on applications of data on the thermal conductivity of metals. Symposium on Effect of Temperature on the Properties of Metals, A.S.M.E.-A.S.T.M., p. 725, 1931.
[3] M. S. Van Dusen and S. M. Shelton, B.S.Jour. Research, vol. 12 (RP 668), p. 439, 1934.

TABLE 1.—*Chemical composition and previous history of materials*

Designation	Material	Chemical composition—percent												History
		T.C.	G.C.	C.C.	C	Mn	P	S	Si	Ni	Cr	W	Al	Ti	
C_1	Basic open-hearth iron				0.02	0.03	0.042	0.005							Hot rolled to 1-inch bar. Tested "as rolled".
C_2	Wrought iron				.04	.046	.136	.025	0.265						Hot rolled to 1-inch bar. Grade A. A.S.T.M. specification A 84-21. Tested in the direction of forging "as rolled".
C_3	Cast iron	3.93	3.34	0.59		.63	.134	.077	1.40						Ingot mold material from cupola furnace. Specimen machined from a sand-cast bar 1.11-inch diam. and tested in the "as cast" condition.
C_4	Cast iron	4.16	3.50	.66		.79	.120	.040	1.35						Ingot mold material from blast furnace. Specimen machined from a sand-cast bar 1.11-inch diam. and tested in the "as cast" condition.
S_1	High-carbon steel				.83	.27	.017	.015	0.16						Specimen machined from hot-rolled rod 1-inch in diameter. Bar was heated to 800 C for 2 hr in an electric furnace and furnace cooled.
S_1Q	Same				.83	.27	.017	.015	.16						After the thermal conductivity determination, specimen S_1 was normalized by heating to 900 C for 10 minutes and air cooled. Reheated to 800 C for 10 minutes and quenched in water at room temperature. Reheated to 250 C, for 1 hr and furnace cooled.
S_2	Low-nickel steel				.35	.56	.015	.020	.02	1.37	0.46				Basic open-hearth steel, poured at 1480 C to an 18 by 21 inch ingot. Hot rolled to 4 by 4 inches, then to a rod 1-inch in diameter. Normalized at 900 C.
S_3	Low-manganese steel				.51	1.65	.016	.023	.24	0.10					Basic open-hearth steel, poured at 1480 C to a 22 by 25 inch ingot. Hot rolled to 4 by 4 inches, then to a rod, 1-inch in diameter. Normalized at 900 C.
S_4	Tungsten steel				.35	0.75	.35	.028	.22	.17	.61	1.04			Acid open-hearth steel, poured at 1490 C to an 18 by 21 inch ingot. Hot rolled to 4 by 4 inches, then to a rod 1 inch in diameter. Normalized at 900 C.

TABLE 1.—*Chemical composition and previous history of materials*—Continued

Designation	Material	Chemical composition—percent													History
		T.C.	G.C.	C.C.	C	Mn	P	S	Si	Ni	Cr	W	Al	Ti	
S_1	Low-chromium steel				0.10	0.45	0.013	0.017	0.18		5.15				Hot rolled to 1½-inch round bar. Annealed.
A_1	Chromium steel				.08	.35	.020	.017	.20	0.05	15.19				Basic electric-furnace steel poured at 1490 C to a 12 by 12 inch ingot. Cogged to 4 by 4 inches, then rolled to a 1-inch round bar. Annealed at 845 C.
A_2	Chromium steel				.07	.09	.015	.010	.09	.23	12.00				Basic electric-furnace steel poured at 1500 C to an 8 by 8 inch ingot. Cogged to 4 by 4 inches, then rolled to a 1-inch round bar. Annealed at 845 C.
A_3	Chromium steel				.14	.19	.020	.015	.12	.70	14.60				Basic electric furnace steel poured at 1500 C to an 8 by 8 inch ingot. Cogged to 4 by 4 inches, then rolled to a 1-inch round bar. Annealed at 845 C.
A_4	High-chromium steel				.10	.40	.013	.008	.45	.18	26.00				Hot rolled to 1½-inch round bar. Annealed.
A_5	Chromium-aluminum steel.				1.10	.30			.47	.35	17.12		1.55		500-lb induction furnace. Poured at 1490 C to 8 by 8 inch ingot. Rolled to 4 by 4 inches, then to a 1-inch round bar. Normalized at 900 C.
A_6	Manganese-nickel steel				0.70–.80	12.–13.				3.00					Machined specimen received. Previous history unknown. (Chemical composition nominal).
A_7	Chromium-nickel steel				.07	.27				9.10	18.6				1-inch round bar. Heated to 735 C, held for 8 hr and cooled in diatomaceous earth.
A_8	Chromium-nickel steel				.11	.19				9.21	18.5				1-inch round bar. Heated to 1120 C and quenched in cold water.
A_9	Chromium-nickel steel				.24	.37				8.96	19.6				1-inch round bar. Heated to 735 C, held for 8 hr and cooled in diatomaceous earth.
A_{10}	Chromium-nickel steel				.24	.28				7.99	19.6				1-inch round bar. Heated to 1120 C and quenched in water.
$A_{10}A$	Chromium-nickel steel				.24	.28				7.99	19.6				After the thermal conductivity determination, specimen A_{10} was heated for 8 hr at 735 C and furnace cooled.
A_{11}	Chromium-nickel-titanium steel.				.07	.59	.013	.003	.47	9.12	18.08			0.34	Hot rolled 1½-inch round bar. Annealed.

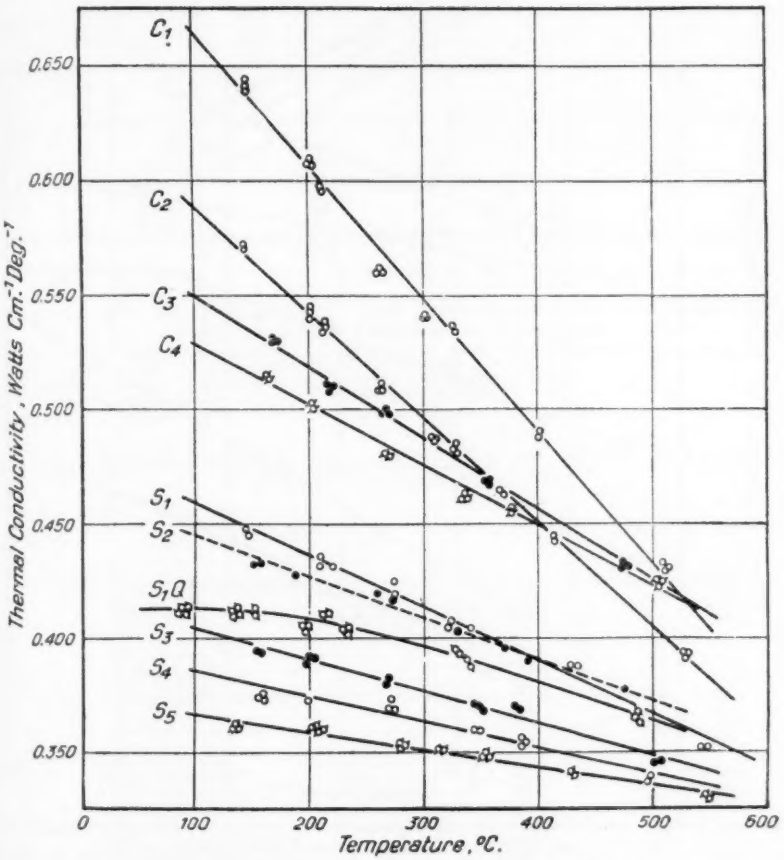

FIGURE 1.—*Thermal conductivity of irons and low alloy steels from 100 to 550 degrees Centigrade (212 to 1,020 degrees Fahrenheit).*

C_1—open hearth iron; approximately 99.9 percent iron.
C_2—wrought iron; approximately 99.5 percent iron.
C_3 and C_4—cast irons; approximately 4.0 percent carbon and 1.5 percent silicon.
S_1 and S_1Q—carbon steel; 0.83 percent carbon.
S_2—nickel steel; 0.35 percent carbon; 1.37 percent nickel; 0.46 percent chromium.
S_3—manganese steel; 0.51 percent carbon; 1.65 percent manganese.
S_4—tungsten steel; 0.35 percent carbon; 1.04 percent tungsten.
S_5—chromium steel; 0.10 percent carbon; 5.15 percent chromium.

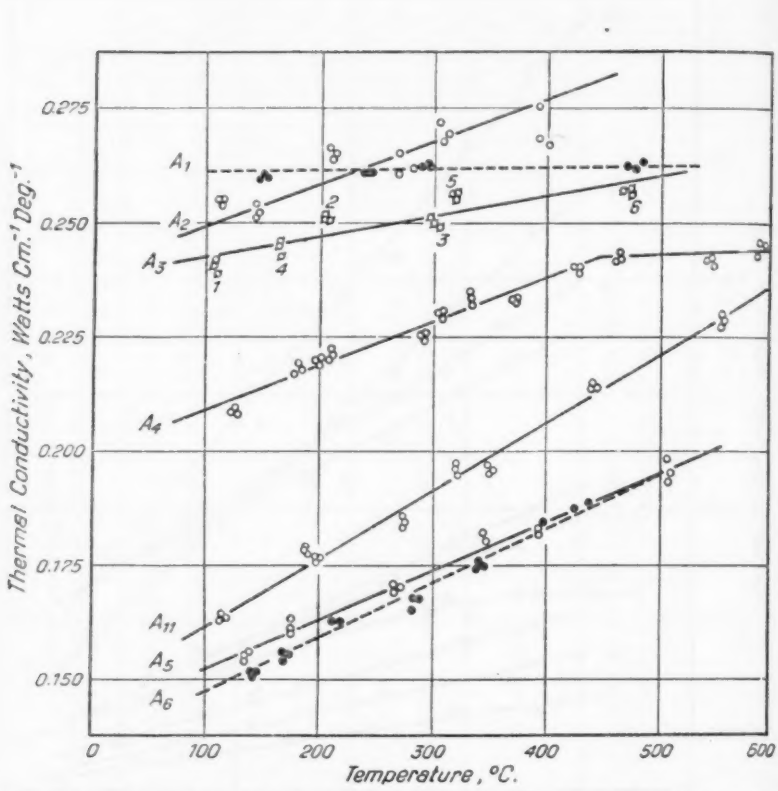

FIGURE 2.—*Thermal conductivity of high alloy steels from 100 to 600 degrees Centigrade (212 to 1,110 degrees Fahrenheit).*

A_1—chromium steel; 0.08 percent carbon; 15.19 percent chromium.
A_2—chromium steel; 0.07 percent carbon; 12.0 percent chromium.
A_3—chromium steel; 0.14 percent carbon; 14.60 percent chromium.
A_4—chromium steel; 0.10 percent carbon; 26.00 percent chromium.
A_5—chromium-aluminum steel; 1.10 percent carbon; 1.55 percent aluminum; 17.12 percent chromium.
A_6—manganese-nickel steel; 0.7 to 0.8 percent carbon; 12 to 13 percent manganese; 3.0 percent nickel.
A_{11}—titanium bearing "18–8" stainless; 0.07 percent carbon; 0.34 percent titanium.

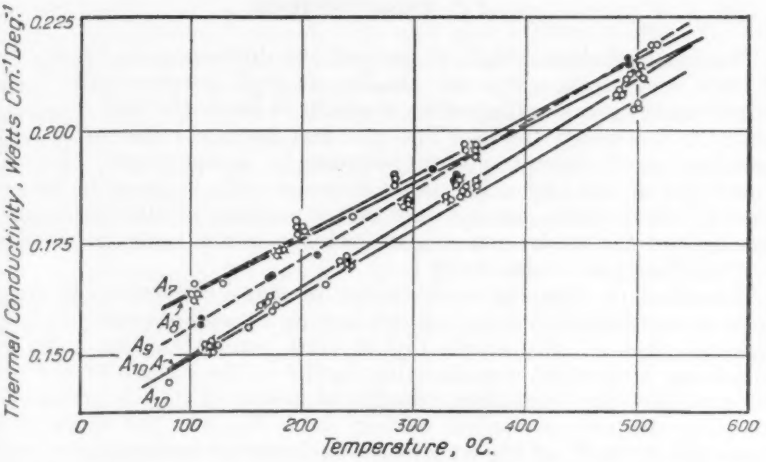

FIGURE 3.—*Thermal conductivity of "18–8" stainless steels from 100 to 550 degrees Centigrade (212 to 1,020 degrees Fahrenheit).*

A_7—0.07 percent carbon; 9.10 percent nickel; 18.6 percent chromium.
A_8—0.11 percent carbon; 9.21 percent nickel; 18.5 percent chromium.
A_9—0.24 percent carbon; 8.96 percent nickel; 19.6 percent chromium.
A_{10} and $A_{10}A$—0.24 percent carbon; 7.99 percent nickel; 19.6 percent chromium.

TABLE 2.—*Thermal conductivity, watts cm^{-1} deg^{-1}, interpolated for the temperatures listed from the experimental results*

Designation	Material	100 C	200 C	300 C	400 C	500 C
C_1	Basic open-hearth iron	0.665	0.607	0.549	0.491	0.435
C_2	Wrought iron	.589	.543	.497	.451	.405
C_3	Cast iron	.550	.519	.488	.458	.426
C_4	Cast iron	.528	.502	.476	.449	.422
S_1	Plain carbon steel	.458	.435	.413	.390	.367
S_1Q	Same, quenched	.412	.408	.396	.381	.364
S_2	Low-nickel steel	.445	.427	.409	.391	.372
S_3	Low-manganese steel	.403	.389	.376	.363	.349
S_4	Tungsten steel	.385	.371	.363	.352	.341
S_5	Low-chromium steel	.366	.358	.351	.343	.336
A_1	Chromium steel	.261	.262	.262	.262	.263
A_2	Chromium steel	.249	.259	.268	.277	----
A_3	Chromium steel	.243	.247	.252	.256	.261
A_4	High-chromium steel	.209	.219	.229	.238	.243
A_5	Chromium-aluminum steel	.177	.188	.199	.210	.221
A_6	Manganese-nickel steel	.148	.160	.171	.183	.195
A_7	Chromium-nickel steel	.164	.177	.190	.203	.216
A_8	Chromium-nickel steel	.163	.176	.189	.201	.214
A_9	Chromium-nickel steel	.156	.172	.187	.202	.217
A_{10}	Chromium-nickel steel	.149	.164	.178	.193	.207
$A_{10}A$	Same, annealed	.150	.166	.181	.196	.212
A_{11}	Chromium-nickel-titanium steel	.161	.176	.191	.206	.221

The values relative to lead are believed to be accurate within 2 percent. Experimental data in the literature indicate that the thermal conductivity of lead at 0 C is known to an accuracy of 3 percent or better. If at any time the thermal conductivity of the lead standard is measured by an absolute method and the present accepted value is found to be in error, the data on all of the materials tested may be corrected by proportionate adjustment.

IV. DISCUSSION

The results indicate that, in general, the differences in conductivity of irons and steels are much smaller at high temperatures than at room temperatures. High-alloy steels have lower thermal conductivities than low-alloy steels. The thermal conductivities of iron and low-alloy steels decrease with increase in temperature. The conductivities of the high-alloy steels increase with increase in temperature; in other words, an increase in the amount of alloying constituents in iron causes, in general, an increase in the temperature coefficient of thermal conductivity.

The effect on thermal conductivity of small differences in composition is more marked in iron alloys having a small amount of alloying elements than in alloys with higher alloy concentrations. An additional and somewhat complicating factor is the nature of the alloy. For example, the total alloy content of cast iron (C_3) is greater than the alloy content of a plain carbon steel (S_1) but the thermal conductivity at 100 C of the cast iron was found to be approximately 20 percent higher than the conductivity of the plain carbon steel at the same temperature. The results on the plain carbon steel (S_1 and S_1Q) show that a heat treatment which resulted in a change in structural constitution produced an appreciable change in conductivity at lower temperatures. The many, and sometimes conflicting, factors concerned make it practically impossible to generalize on the quantitative relationship of thermal conductivity and total alloy content of ferrous metals.

With the exception of quenched plain carbon steel (S_1Q), the thermal conductivities of all the materials tested were found to be linear functions of temperature within the range of temperature in which measurements were made. An unusual "scatter" is noticeable in the plotted points representing the determinations on the chromium steel (A_2). The differences are irregular in character and the most probable explanation is that a structural change in the specimen took place with repeated heating in the apparatus. The irregular character of the "scatter" supports the belief that it cannot be attributed to experimental error. A typical example of "scatter" evidently due to experimental error or to a lack of homogeneity of the specimen is shown by the points representing the determination on steel A_3. The results of the first series of determinations at relatively low temperatures are represented by the groups of points numbered 1, 2, and 3 (fig. 2). The results of the second series at relatively high temperatures are represented by the groups 4, 5, and 6. The character of the "scatter" is the same for both series although the temperatures were quite different. A more complete investigation over a wider range of temperature is desirable but was not possible in the present apparatus.

The "18–8" chromium-nickel steels studied represent low-carbon steels (0.07 to 0.11 percent) in the annealed condition (A_7) and in the quenched condition (A_8) and high-carbon steels (0.24 percent) in the corresponding conditions annealed (A_9) and quenched (A_{10}). As shown by the curves in figure 3, the results on the two low-carbon steels coincided within the experimental error at low temperatures, and very nearly so at higher temperatures. The higher carbon specimens showed differences in both thermal conductivity and tempera-

ture coefficient over the whole temperature range. A greater difference in composition existed between the two high-carbon steels. In order to determine whether the differences in thermal conductivity of the high-carbon steels could be attributed to composition or to previous heat treatment, the quenched specimen was annealed and the thermal conductivity was redetermined. According to the results, the thermal conductivity of the reannealed steel was unchanged at low temperature, but at higher temperatures the annealed material had a higher conductivity than the quenched material. It is noteworthy, and possibly of some significance, that the thermal conductivity of the annealed steel was practically the same as that in the quenched state, but the temperature coefficient of the reannealed specimen $A_{10}A$ was of the same order of magnitude as that of the annealed specimen (A_9) of a different composition.

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WASHINGTON, July 22, 1933.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP670

Part of Bureau of Standards Journal of Research, vol. 12, April 1934

COMPARATIVE PERFORMANCE OF WATCHES WITH ELINVAR AND WITH STEEL HAIRSPRINGS

By Ralph E. Gould

ABSTRACT

The performance of watches having the usual cut, bimetallic balance wheels and steel hairsprings is compared with that of watches having uncut, monometallic balance wheels and elinvar hairsprings. The latter combination of vibrating assembly is a new application intended to improve the general performance of watches.

Twenty watches of each type, 10 each of 2 makes, were given performance tests at temperatures encountered in ordinary use. The temperature-rate errors of the watches having the new vibrating assembly were less than those for watches having the ordinary assembly, and instead of the usual parabolic curve, a curve approaching a straight line was obtained. Marked improvement in performance at temperatures within the usual temperature range 5 to 35 C is indicated by the use of the new assembly.

The new assembly almost entirely overcomes the effects of magnetism so that, after the watch is removed from a magnetic field, the rate is not subject to fluctuations experienced with the ordinary assembly.

There is no evidence of any marked difference in performance of the two types of watches in different positions or for isochronism.

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I. INTRODUCTION

The rate [1] of a watch is affected by change in temperature to the same degree as is the free period of its vibrating assembly, which consists of the balance wheel with its hairspring and staff. In the usual design of the assembly, a steel hairspring is used. The effect of its change in stiffness with change of temperature upon the free period of the assembly is compensated by a change in moment of inertia of the balance wheel. The rim of the balance wheel is bimetallic (brass and steel) and is cut at 2 diametrically opposite points (fig. 1) so that a change in shape may take place as a result of unequal expansion of the 2 materials.

Watches with a new form of vibrating assembly have recently been placed on the market. In this assembly the hairspring is made of a nickel-steel alloy known as "elinvar" which has a temperature coefficient of elasticity which is very nearly 0 within the usual temperature range (5 to 35 C). With this hairspring an uncut, monometallic

[1] Rate or daily rate is the number of seconds lost or gained in 24 hours.

balance wheel (fig. 1), of nonmagnetic material, is used in place of the cut, bimetallic balance wheel.

Tests were made to determine the comparative performance of watches equipped with the usual vibrating assembly and of those equipped with the new assembly. Twenty watches of each type and

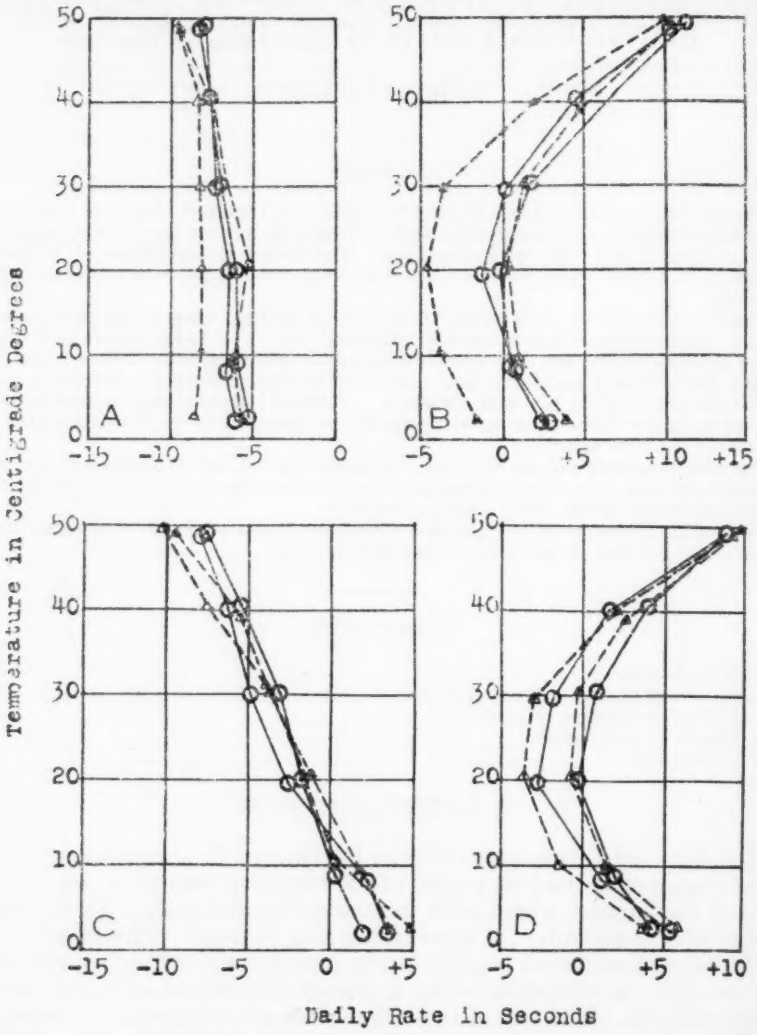

FIGURE 2.—*Temperature-rate curves.*

A and C. Watches having monometallic balance wheels and elinvar hairsprings. B and D. Watches having bimetallic balance wheels and steel hairsprings. Each diagram is the composite curve for 10 similar watches of the same make. A and B represent watches of one make, while C and D represent those of another make.

of two different makes were tested at different temperatures, and in various positions. The effect of isochronism on these watches was determined. Three watches of each type were placed momentarily in magnetic fields of known intensity, and the rates determined after subjection to each field strength.

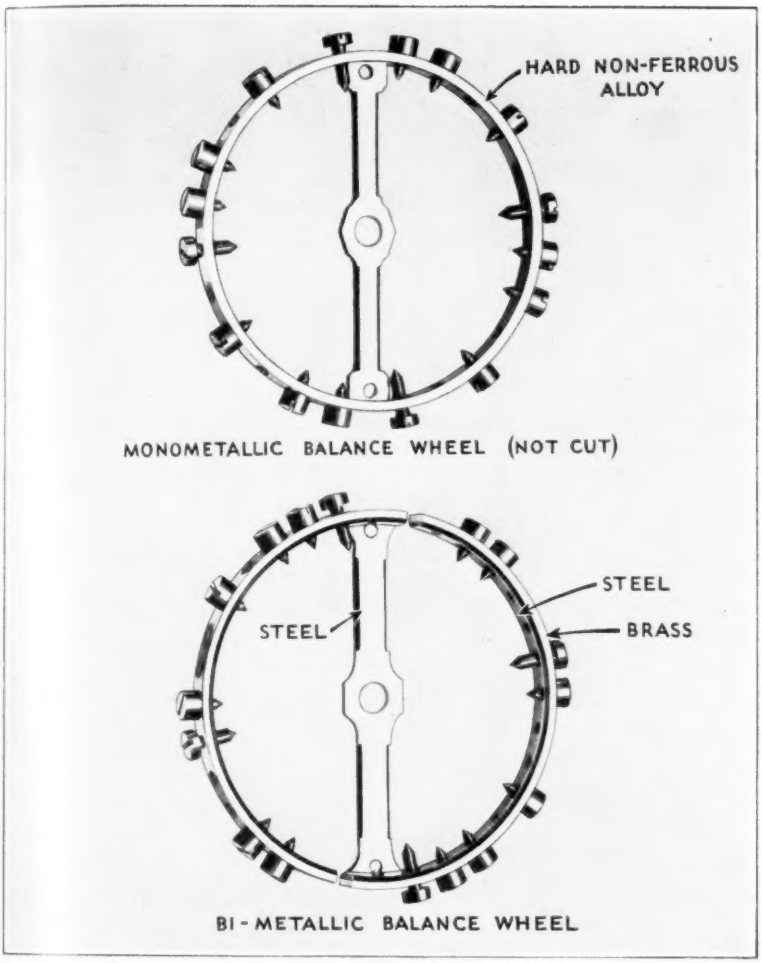

FIGURE 1.—*The new and old balance wheels.*

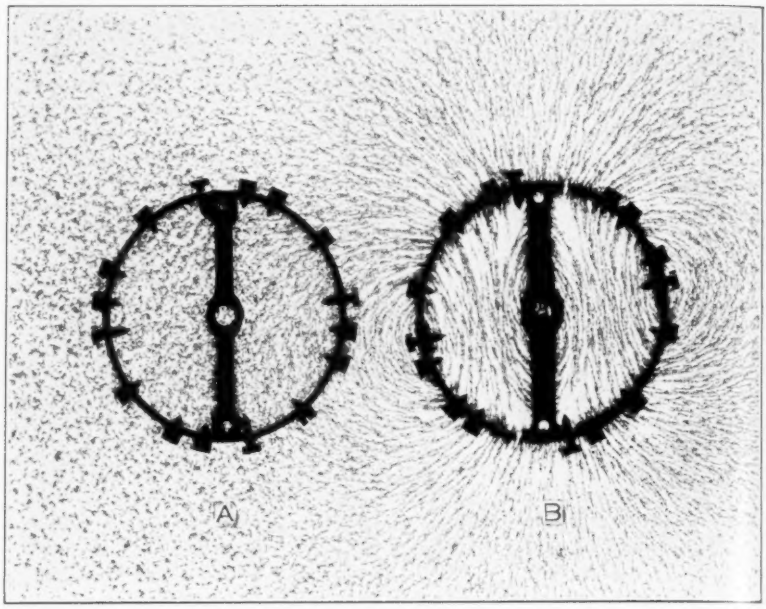

FIGURE 4.—*Magnetic condition of the balance wheels after removal from a magnetic field.*

A, Monometallic balance wheel; B, bimetallic balance wheel.

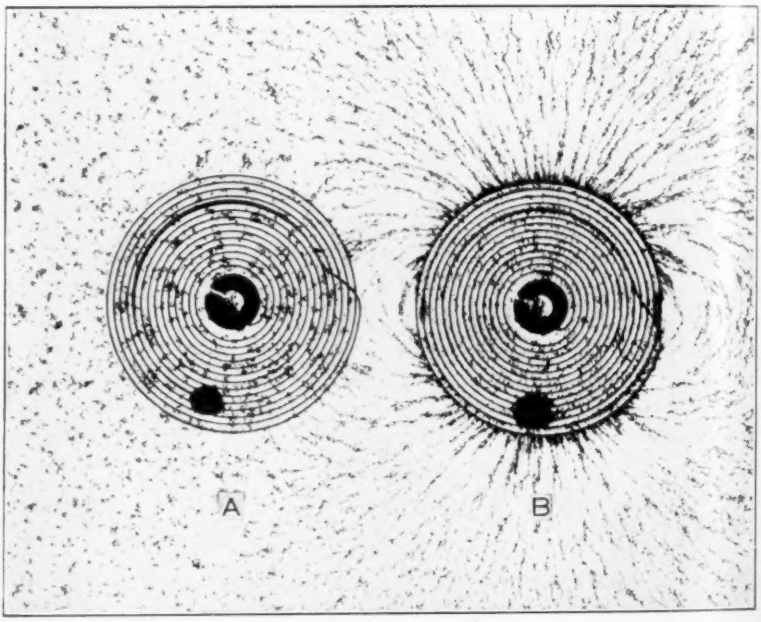

FIGURE 5.—*Magnetic condition of the hairsprings after removal from a magnetic field.*

A, Elinvar hairspring; B, steel hairspring.

II. EFFECTS OF CHANGES IN TEMPERATURE

The effect of changes in temperature on the daily rates of 20 watches of each of the 2 types was determined. The watches were placed in a testing chamber in a horizontal, dial-up position and were simultaneously subjected to 2 temperature cycles from 0 to 50 to 0 C. The temperature was varied by steps of approximately 10 C. The watches were kept at each temperature for 2 days, and the daily rate was taken as the mean of the rates for the 2 days. Whenever the temperature was changed, the rate for that day was not used in computing the mean rate. Figure 2 shows the results of this test.

An inspection of the curves shows that the temperature-rate curves for watches with the ordinary vibrating assembly are parabolic in form, while those for watches with the new assembly are approximately straight lines. The slope of these straight lines, or the change in rate per degree C, indicates the degree of temperature compensation of the watch. Because of the parabolic form of the curve, watches using the bimetallic balance wheel and steel hairspring show a considerable difference between the middle temperature (20 C) rate and those at the high (35 C) and low (5 C) temperatures. With the new balance wheel and hairspring these differences are much reduced and indicate that with careful adjustment they may be practically eliminated.

The curves for the second cycle (triangles) do not coincide with those for the first cycle (circles), but have an appreciable displacement. Examination was made of the shellac which helps to hold the pallet jewels [2] in their mountings and of the oil used in lubricating the watch. While the shellac showed a slight softening at temperatures above 45 C, there was no evidence of shifting of the jewels. The oil on several of the watches showed some signs of deterioration or gumming.

III. EFFECTS OF CHANGES IN POSITION

The 40 watches, mentioned above, were tested to determine whether or not any improvement in uniformity of rate in different positions resulted from the use of the new assembly. To eliminate any effect of temperature variations, the test was conducted at a constant temperature of 20 C. The watches were mounted firmly in holders on a frame which could be turned about different axes. The axes used were (1) one parallel to the hand staff of the watch, (2) one parallel to the 9–3 line of the dial, and (3) one parallel to the 12–6 line of the dial. The pendant in all cases was at the 12 point.

The rotation about an axis parallel to the hand staff was begun with the watches vertical, 12 up, dial front. The frame, with the watches, was rotated to the left through a complete revolution in steps of 15 degrees a day.

The rotation about an axis parallel to the 9–3 line was begun with the watches horizontal, dial up, 12 back. The frame was rotated forward in steps of 15 degrees a day.

The rotation about an axis parallel to the 12–6 line was begun with the watches horizontal, dial up, 12 back. The frame was rotated to the left in steps of 15 degrees a day.

[2] Pallet jewels are the jewels which serve as rolling contact surfaces in transmitting the action of the balance wheel to the escape wheel.

Daily rates were computed for each position of the watches and, because of close agreement in performance of the two makes of watches, composite curves (fig. 3) were plotted only for each axis of rotation. The general forms of the curves conform to those expected on the basis of the ideas advanced by Kleinlein,[3] Gribi,[4] and others, and depend upon the relative locations of the inner and outer pinning points of the hairspring. From the forms of these curves it appears that no material change in performance with change of position results from the use of the new vibrating assembly.

IV. EFFECTS OF MAGNETISM

The accuracy of the ordinary watch having a bimetallic balance wheel and a steel hairspring is greatly affected by magnetism. When

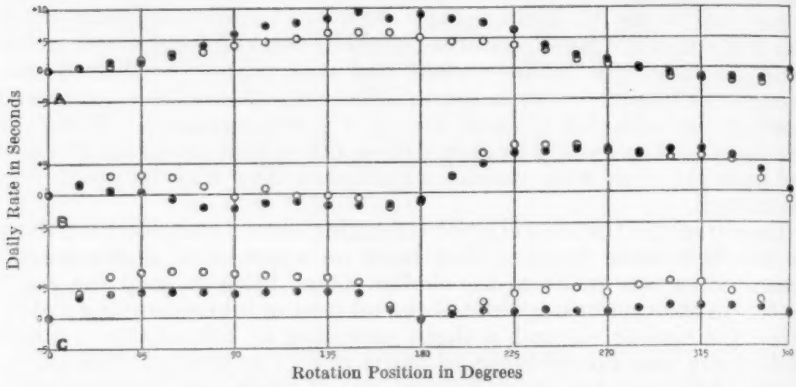

FIGURE 3.—*Position-rate curves.*

A. Rotation on an axis parallel to the hand staff; B. Rotation on an axis parallel to the 9–3 line; C. Curve for rotation on an axis parallel to the 12–6 line. The circles are composite values for 20 watches of 2 makes having monometallic balance wheels and elinvar hairsprings. The dots are composite values for 20 watches of 2 makes having bimetallic balance wheels and steel hairsprings.

placed in a strong magnetic field the steel hairspring and the balance arm become permanently magnetized; the hairspring is drawn out of place, sometimes even touching the balance arm; and the watch performs very erratically. The only remedy is a thorough demagnetizing of the watch.

Since elinvar has a temperature coefficient of elasticity which is nearly 0 within the usual temperature range, a cut bimetallic balance wheel is not needed for temperature compensation and an uncut wheel of nonmagnetic material may therefore be used. Also the elinvar hairspring, although it can be magnetized, does not retain its magnetism when the watch is removed from the magnetic field, and the performance of the watch is not permanently changed.

The magnetic conditions representative of the two types of balance wheels and hairsprings, after having been subjected to a magnetic field, are shown in figures 4 and 5.

The rates of three watches of each type were determined after being subjected to magnetic fields of known strengths. These fields were

[3] W. J. Kleinlein, Practical Balance and Hairspring Work, and Rules and Practice of Adjusting Watches, W. J. Kleinlein, Comstock Building, Columbus, Ohio.

[4] Theo. Gribi, Practical Course in Adjusting. Jewelers' Circular Publishing Co., New York, N.Y., 1901.

produced by a solenoid for which the field strength at the center is given by the formula:

$$H = KI$$

in which

H = field strength in oersteds [5]

K = an experimentally determined constant, in this case 88.5

I = current in amperes

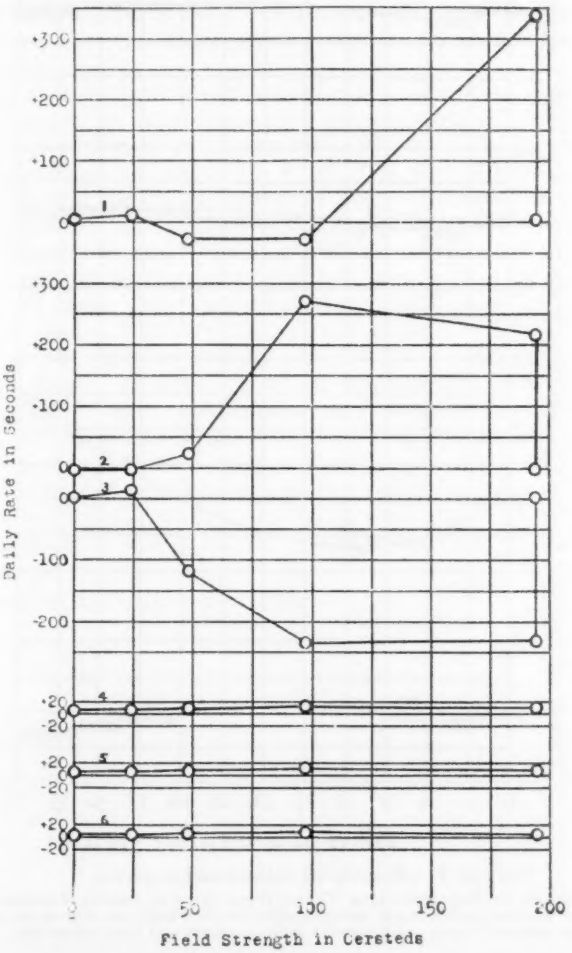

FIGURE 6.—*Performance after subjecting watches to a magnetic field.*

Curves 1, 2, and 3 are for watches having cut bimetallic balance wheels and steel hairsprings. Recovery of the original rate after demagnetization is shown by the last circle on the right, near the zero line. Curves 4, 5, and 6 are for watches having uncut, monometallic balance wheels and elinvar hairsprings.

The field strengths used were 24.3, 48.2, 97.4, and 194.7 oersteds.[6]

[5] A field strength of 1 oersted produces in empty space a magnetic induction of 1 gauss (sometimes called 1 line of force per square centimeter).

[6] An idea of the relative values of the field strengths used may be gained from the fact that in the vicinity of Washington, D.C., the horizontal component of the earth's magnetic field is of the order of 0.2 oersted and the magnetic field close to an electric locomotive is approximately 50 oersteds.

Before placing the watches in the magnetic field, their daily rates were obtained. They were then placed in the magnetic field of lowest strength for a few seconds, after which the daily rates were again obtained. Without demagnetizing, this procedure was repeated for increasing values of the magnetic field strength. After determining the daily rate for the highest field strength used, the watches were

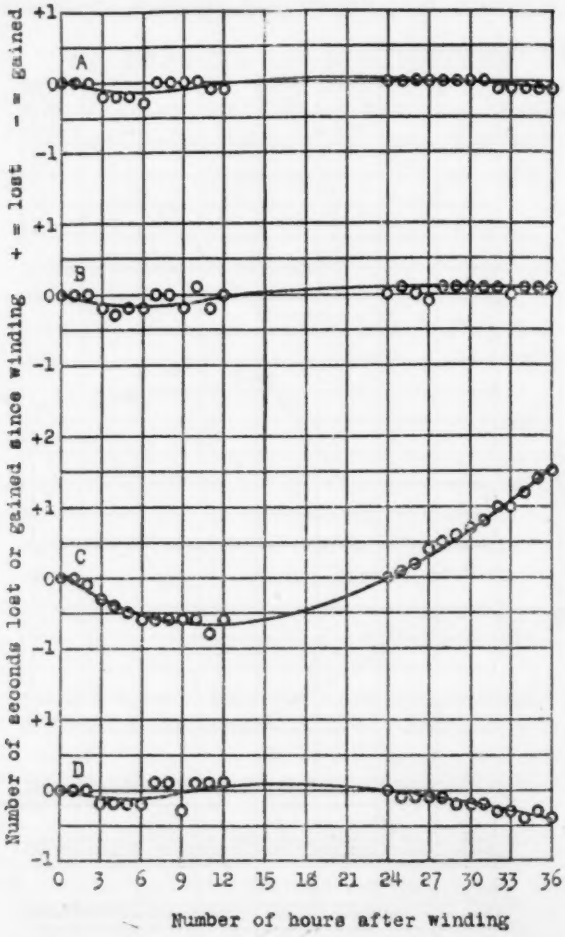

FIGURE 7.—*Isochronal rate variation curves.*

Curves A and B are for watches of one make. Curves C and D are for watches of another make. Curves A and C are for watches having uncut, monometallic balance wheels and elinvar hairsprings. Curves B and D are for watches having cut, bimetallic balance wheels and steel hairsprings.

demagnetized by placing them in an alternating magnetic field of approximately 165 oersteds.

The daily rates of these watches after each change of field strength are shown in figure 6. These curves show a wide variation in performance for the three watches of the ordinary type, while they show practically no change in rate for watches having the new vibrating assembly.

The new balance wheel, therefore, is a decided improvement over the old one in overcoming the effect of magnetic fields in which it may happen to be temporarily placed.

V. ISOCHRONISM [7]

Very few watches maintain an absolutely uniform rate as the mainspring unwinds. If rate be plotted against time after winding, true isochronism may be represented by a straight line drawn from the point representing the 24-hour rate to the 0 point. If the variation from this line of the rates observed at different intervals after winding be plotted, on the same basis as for the aforementioned curve, the resulting curve will show how closely the watch has been adjusted to isochronism.

The 40 watches, previously mentioned, were tested for 36 hours after winding, while maintained in the horizontal, dial-up position and at a temperature of approximately 20 C. The curves of figure 7 were obtained from the results. Curves *A* and *B* represent watches of the 2 types of 1 make, and curves *C* and *D* those of the same types of another make. Each curve is the component curve for 10 similar watches. Curves *A* and *C* are for watches having the new vibrating assembly, and curves *B* and *D* are for watches having the old assembly.

The curves show very close agreement and close adjustment for *A*, *B*, and *D*, but a much greater variation for *C*. The shapes of the curves beyond the 24-hour point are of little consequence as watches are usually wound at intervals of, or reasonably close to, 24 hours. The new assembly does not appear to give any material advantage in the matter of isochronism over the old assembly. Watches of both types may be adjusted to give about the same isochronal results.

The author wishes to acknowledge the valuable assistance rendered, in connection with the work reported in this paper, by H. L. Beehler, of the Hamilton Watch Co., and by A. B. Cook, of the Bureau of Standards.

WASHINGTON, February 24, 1934

[7] Isochronism is the uniformity of rate as the mainspring unwinds.

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FIRST SPECTRUM OF TANTALUM

By C. C. Kiess and E. Z. Stowell

ABSTRACT

Wave lengths of more than 2,100 lines emitted by the arc in air between electrodes of tantalum metal have been measured in the spectral region from 10,300 A in the infrared to 2,300 A in the ultraviolet. These lines are characteristic of the spectrum emitted by neutral tantalum atoms. Many of the lines are clearly complex and present the appearance of narrow rectangles. Several lines in the ultraviolet, which have been found to originate in the lowest energy state, were observed as absorption lines in the spectrum of the underwater spark. The arc spectrum is always accompanied by an extensive band spectrum, attributable to the oxide, which consists of bands shaded toward the red from inconspicuous heads. Whenever recognized as such, these heads have been measured.

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I. INTRODUCTION

The properties of a chemical element, which must be known in order to understand its physical and chemical behavior, now include a tabulation of its atomic energy states as revealed by analyses of the term structures of its spectra. But analysis of the term structure of a spectrum, especially if it is complex, requires an accurate and extensive list of wave lengths together with such descriptive features of the individual lines as intensity, Zeeman effect, reversibility, hyperfine structure, and others.

For the element tantalum, atomic number 73, which has been known to chemists for more than a century, only 13 papers descriptive of its spectra were listed by Kayser in volume 6 of the Handbuch der Spectroscopie. In the interval that has elapsed since the publication of this work in 1912, numerous papers on the tantalum spectra have appeared, but most of these deal with the X-ray spectra and only a few with the optical spectra. In 1917, Frl. Josewski [1] published new wave-length measurements in the range from 2,427 A in the ultraviolet to 7,007 A in the red. Although her work did not extend our knowledge of tantalum spectra beyond the limits reached in the earlier investigations, nevertheless it furnished an accurate scale of wave lengths from which corrections for the earlier measurements could be derived. In 1927, Allin and Ireton [2] published a list of ultraviolet tantalum lines which they observed as absorption lines in the spec-

[1] Zeit. wiss. Phot., vol. 17, p. 79; 1917.
[2] Trans. Roy. Soc., Canada, sec. 3, vol. 21, p. 127, 1927.

trum of the underwater spark; and in 1928 McLennan and Durnford [3] published some measurements of the Zeeman effect for tantalum lines lying between 5,519 and 6,675 A. Quite recently, brief notes have appeared by: (1) Kiess and Kiess, [4] who give a preliminary list of terms for the spectrum of neutral tantalum atoms; (2) Gisolf and Zeeman [5] who report measurements of the hyperfine structure of certain lines of tantalum and a value of 7/2 for its nuclear moment; (3) McMillan and Grace, [6] who likewise have measured hyperfine structures and have found a nuclear moment of 7/2.

Investigation of the tantalum spectra was begun at the Bureau of Standards more than 10 years ago when it was realized that the first requisite for a successful analysis of the term structure of a complex spectrum is an extensive and accurate list of its wave lengths. It was planned, therefore, to photograph the spectra emitted by tantalum arcs and sparks throughout the domain accessible to us with the spectrographs and photographic materials at our disposal, and to supplement this survey with observations of the Zeeman effect and of the underwater spark. The observational work involved in this program is practically completed but much still remains to be done in the way of measurement and calculation. In this paper, we present a list of the lines we have measured in the spectrum emitted by neutral tantalum atoms, together with estimates of their intensities and descriptions of certain characteristics we have noted for them. In subsequent papers it is planned to present the results obtained from work now in progress for the spectra emitted by ionized atoms, for the Zeeman effect, and for the term structures of the spectra.

II. EXPERIMENTAL PROCEDURE

The spectrograms on which this investigation is based were secured with the grating and prism spectrographs of the Bureau of Standards. The gratings and their mountings have been described in previous papers.[7] The prism spectrograph, constructed by Hilger, is new, and is believed to be the most powerful instrument of its kind in existence. It is provided with two quartz prisms—one a 60° Cornu prism, and the other a 30° reflecting prism—with faces measuring 12 by 20 cm. The instrument is mounted in the Littrow style, the lens being 12 cm in diameter. Between 2,100 and 3,000 A the dispersion of this spectrograph varies from 0.4 to 2 A per mm.

The prism spectrograph was used in photographing the ultraviolet portions of the tantalum spectra between 2,100 and 3,100 A. The various grating spectrographs were used from 2,200 A to the limit reached at 10,300 A in the infrared. For the regions from 2,200 to 2,900 A and from 5,000 to 9,000 A the first order of the 20,000 lines-per-inch grating, giving a dispersion of 3.6 A per mm, was used. The second order of this grating was used for the plates covering the interval from 2,900 to 5,000 A. For the infrared regions of the spectrum the Anderson grating, giving a dispersion of 10 A per mm, was used.

In making a spectrogram, the light from the arc and from the spark discharge between electrodes of the same metal, was photographed in juxtaposition on two strips of the plate. Adjacent to these were

[3] Proc. Roy. Soc., London, vol. A 120, p. 502, 1928.
[4] B.S., Jour. Research, vol. 11 (RP589), p. 277, 1933.
[5] Nature, vol. 132, p. 566, 1933.
[6] Phys. Rev., vol. 44, p. 325, 1933; and vol. 44, p. 949, 1933.
[7] B. S. Scientific Papers nos. 312, 441, and 499.

exposures to the iron arc to furnish the standard scale used in the wave-length determinations. The spark exposures were faint, however, and revealed no lines other than the strongest arc lines in the regions longer than 3,700 A. Consequently, no attempt was made in this investigation to photograph the spark spectrum to waves longer than 5,000 A. To photograph the regions not readily recorded with ordinary plates, special plates were used. These comprised: (1) Schumann plates, prepared according to the recommendations of Hopfield and Appleyard; [8] (2) plates sensitized to the green, yellow, red, and near infrared by bathing them in suitable dye solutions according to our usual practice; [9] and (3) the new infrared plates brought out by the Eastman Kodak Co.[10]

The material used as electrodes in the arcs and sparks was metallic tantalum kindly sent to us for this investigation by C. W. Balke [11] of the Fansteel Co., who has described its preparation. The arcs were maintained by direct currents of 5 to 10 amperes supplied by 220-volt mains. The sparks were maintained by a battery of condensers of 0.006 μf capacity which were charged by transformers of either 10,000 or 40,000 volts, stepped-up from the 110 volt ac circuit. The tantalum arc in air has a tendency to flicker, and, after molten beads of the oxide have formed on the electrodes, the ends of the arc travel along the electrodes away from oxide beads which soon solidify. The oxide when cool is nonconducting and it is necessary to bring the electrodes into contact repeatedly in order to maintain the arc. Furthermore, a dense cloud of hot oxide particles surrounds and pervades the arc so that the line spectrum in regions longer than 2,400 A is always superposed on a continuous spectrum.

III. RESULTS

Our measurements of the tantalum spectra have yielded a list of 2,100 lines which, we believe, are emitted by neutral atoms. All lines recognized as emitted by ionized atoms have been omitted from the list which is presented in table 1. Except for a few lines each recorded wave length is the mean of 2 to 6 accordant measurements made, for the most part, by 2 observers. The reference lines, chosen from the iron spectrum, were the adopted international secondary standards in the regions where these are available. In the ultraviolet where no secondary standards have yet been adopted Burns' [12] values of the iron lines, determined by interference methods, have been used. The arc in air emits an extensive band spectrum attributable to the oxide of tantalum. These bands are shaded toward the red from heads which are not very prominent. Whenever recognized as such these heads have been measured and their wave lengths are included in table 1, where they are designated by a letter *n*.

Early in the work of measurement, it was noticed that many of the tantalum lines are not sharp and fine but present the appearance of narrow rectangles. Some of these wide lines exhibit nearly uniform intensity distribution from one edge to the other which is indicated in the table by the letter *b*. Others show partial resolution into hyperfine structure, which is indicated by the letters *c* and *d*. Lines

[8] Jour. Opt. Soc. Amer., vol. 22, p. 488, 1932.
[9] B. S. Scientific Papers, no. 422, vol. 17, p. 353, 1921.
[10] Jour. Opt. Soc. Amer., vol. 23, p. 229, 1933.
[11] Chem. Met. Eng., vol. 27, p. 1271, 1922. Ind. Eng. Chem., vol. 15, p. 560, 1923; and vol. 21, p. 1002, 1929.
[12] Compt. rend., vol. 160, p. 243, 1915; Publ. Allegheny Obs., vol. 6, p. 180, 1929; and vol. 8, p. 43, 1931.

marked with *c* are made up of several components, and many of them exhibit flag-shaped patterns; lines designated with *d* present the appearance of close doublets. The letters *l* and *v* indicate, respectively, that the lines are shaded toward longer or shorter wave lengths. In all cases of complex lines, the recorded wave length is a mean value and refers either to the geometrical center of the rectangular line or to the maximum of intensity, indicated on the spectrograms by the protrusion of an astigmatic tail into the iron comparison spectrum. The letter *r* indicates lines that are absorbed in the under-water spark. Most of the lines so designated are intense and lie in the ultraviolet. They have been found to be related to the basic term, ^{4}F, of the spectrum. It is to be noted that none of them agree with the under-water spark lines recorded by Allin and Ireton for tantalum.

Although the tantalum metal used for electrodes was the purest that had ever been prepared in quantity, yet it was found to contain several impurities of which the most prominent was its analogue columbium. The other impurities, present only in very minute quantity, were tungsten, iron, nickel, silicon, and tin. In the "Revision of Rowland's Preliminary Table of Solar Spectrum Wave-Lengths", St. John[13] lists tantalum among the elements not at that time identified in the sun. It is of interest to note that its presence in the sun is now revealed by the agreement of several of its strongest lines with hitherto unidentified faint solar lines. Among these are the three at 5,997, 5,944, and 5,939 A, which have their origin in the metastable ^{6}D term of Ta I.

TABLE 1.—*Wave lengths in the first spectrum of tantalum*, Ta I

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
10,325.70	2	9,569.57	15	8,936.51	4	8,088.94	2	7,758.23	2
10,303.71	1	9,523.75	3	8,932.63	8	8,076.49	1	7,757.61	2
10,210.90	3	9,512.70	3	8,924.91	2	8,069.05	4	7,733.70	2
10,198.70	1	9,487.20	2	8,834.75	4	8,058.96	1	7,725.09	4
10,195.97	2	9,453.52	3	8,819.58	2	8,053.96	2	7,722.03	10
10,187.99	2	9,438.55	4	8,757.65	1	8,039.11	7	7,719.19	3
10,099.41	15	9,423.80	4	8,721.88	2	8,029.04	2	7,715.03	3
10,079.45	3	9,423.12	2	8,709.00	1*b*	8,026.49	12	7,699.14	5
10,043.27	5*n*	9,288.15	3*b*	8,704.02	1	8,022.09	2	7,690.35	3
9,989.75	5*n*	9,272.63	10	8,652.99	1*b*	7,998.75	2	7,676.24	3
9,971.26	4*n*	9,259.69	4	8,645.60	1*b*	7,996.74	1	7,670.28	7*c*
9,957.94	4*n*	9,254.95	2	8,595.86	7	7,955.54	2*b*	7,650.42	3
9,954.68	4*n*	9,246.16	6	8,583.37	1	7,952.19	2	7,649.62	8
9,941.50	10	9,242.70	5*n*	8,575.92	8	7,950.24	15	7,640.84	4
9,919.90	8*n*	9,231.20	3	8,560.42	1	7,926.58	1	7,625.97	3
9,902.74	5*n*	9,197.40	8*n*?	8,551.91	1	7,921.65	1*n*?	7,622.64	3*b*
9,868.62	25*n*	9,196.05	4*n*	8,550.51	5	7,887.39	1	7,620.84	3
9,849.37	15*n*	9,126.22	1	8,447.62	10	7,882.37	25	7,604.81	2*b*
9,840.33	3	9,123.07	3	8,415.73	3	7,856.48	1	7,593.62	3
9,827.36	3	9,105.70	5	8,413.85	1	7,842.76	15	7,591.38	2*d*?
9,818.67	4	9,088.85	1	8,391.08	1	7,819.57	2	7,590.22	7
9,784.54	8	9,082.30	1	8,389.17	2	7,818.82	2*b*	7,569.18	5
9,780.93	4	9,038.60	1*b*	8,382.25	1	7,815.47	10	7,553.97	4
9,680.75	2	9,032.05	3*b*	8,281.65	20	7,814.00	18	7,541.96	2
9,645.53	20	9,021.60	1	8,264.90	6	7,799.51	4	7,520.56	15
9,640.92	3*d*?	9,008.78	1	8,248.99	4	7,788.95	3	7,515.18	7*b*
9,634.27	4	8,984.70	3	8,180.81	1	7,788.64	2	7,495.31	5
9,608.74	3	8,977.19	1	8,158.53	2	7,779.68	12*b*	7,492.74	3
9,596.75	2	8,975.41	1	8,128.77	3	7,773.52	2	7,490.06	2*b*
9,590.83	1	8,946.15	1	8,100.11	2	7,763.10	10	7,486.55	2

[13] Carnegie Inst. of Washington, Pub. no. 396, p. XX; 1928.

TABLE 1.—*Wave lengths in the first spectrum of tantalum*, Ta I—Continued

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
7,486.01	12	7,025.02	20	6,691.45	1	6,360.84	15	6,133.89	2
7,482.36	2	7,013.92	3	6,684.00	10	6,356.16	18*b*	6,131.21	4
7,471.99	7*c*	7,006.95	25	6,675.53	25	6,351.22	4	6,129.64	2
7,469.05	4	7,005.92	4	6,673.72	20	6,345.99	10	6,126.79	2
7,467.71	12	7,005.05	15	6,669.01	4	6,341.17	12	6,122.92	1
7,460.80	4*d*?	7,003.09	2	6,662.29	8*c*, *l*	6,340.01	3*b*	6,106.51	3
7,454.38	3*b*	7,000.20	8	6,639.41	3	6,332.89	10	6,101.56	12
7,440.14	10	6,995.35	20*d*?	6,632.17	2	6,327.41	2	6,099.96	2
7,435.16	6	6,983.52	7	6,626.15	4*b*	6,326.62	5	6,093.56	2
7,418.86	4	6,981.99	3*d*?	6,621.29	20	6,325.09	15	6,092.95	2
7,410.60	2	6,977.66	3	6,611.91	25	6,321.51	2*b*	6,092.07	5
7,407.87	25	6,971.50	15*c*	6,605.86	3	6,312.22	9	6,091.44	3*b*
7,404.93	2	6,969.49	7	6,587.16	6*b*	6,309.59	18	6,090.81	7
7,389.03	2	6,966.14	25	6,585.09	6	6,309.07	10	6,087.92	1
7,371.03	2	6,957.67	2	6,580.51	1	6,289.33	12	6,087.11	3*b*
7,369.12	20	6,953.86	10	6,578.96	3*d*,?	6,287.91	10	6,084.71	4
7,356.94	18	6,951.23	15	6,577.57	4*b*	6,287.36	8	6,071.75	1
7,355.41	4	6,950.05	4	6,577.12	5	6,283.02	5	6,070.57	4
7,352.87	25	6,946.88	10	6,574.84	18	6,281.36	12*b*	6,059.34	5*c*
7,346.37	30	6,939.33	5	6,570.27	1	6,280.53	2	6,053.70	8
7,343.32	2	6,936.05	2	6,568.23	1	6,278.34	12	6,047.25	18
7,340.14	6*c*	6,928.53	25	6,564.27	10*c*	6,277.55	2*b*	6,045.38	30
7,333.04	2*d*?	6,927.37	20	6,563.72	2	6,274.30	3	6,038.27	2
7,325.94	7	6,919.38	1	6,561.60	10	6,272.52	2*b*	6,034.96	2
7,322.71	10*b*	6,910.47	1	6,559.71	2	6,271.35	1	6,023.37	3
7,319.82	10	6,902.07	20	6,559.26	4	6,268.70	25	6,020.72	18*c*
7,313.18	3	6,900.54	12	6,556.88	2	6,266.38	7	6,019.07	2
7,301.74	25	6,896.76	9	6,547.24	4	6,262.31	2	6,015.90	8
7,296.30	12	6,892.53	3*b*	6,530.70	1	6,258.72	5*b*	6,012.55	5
7,293.80	1	6,888.34	2	6,527.04	4	6,256.68	20	6,009.92	10
7,286.35	7	6,877.46	10	6,516.14	20	6,254.66	8*c*, *v*	6,007.43	2
7,284.43	2	6,875.24	25	6,514.40	20	6,254.16	2	5,999.24	3
7,277.54	6	6,867.33	2*b*	6,505.52	15	6,249.81	10	5,998.21	2
7,276.95	15	6,866.23	25	6,502.43	12	6,247.33	2	5,997.24	35*c*
7,272.25	5	6,865.10	5	6,500.40	2	6,244.47	7*c*	5,974.12	3
7,264.82	12	6,860.78	3	6,486.08	8	6,239.19	5	5,960.12	7
7,250.27	20	6,850.78	8	6,485.36	30	6,238.04	1	5,958.98	2
7,233.46	8	6,833.73	2	6,479.93	3	6,228.01	3	5,958.24	1
7,226.40	3	6,833.24	4	6,472.84	2	6,225.81	1	5,951.78	8
7,207.86	5*b*	6,831.97	6	6,459.91	10	6,223.62	4	5,944.01	30*d*?
7,196.23	3	6,824.94	5*b*	6,459.07	4	6,222.69	2	5,939.75	20*b*
7,191.34	9	6,819.33	7	6,457.38	3	6,221.33	2	5,935.53	5
7,177.42	3	6,813.24	25*c*	6,455.83	5	6,218.98	5	5,931.68	6
7,175.74	5	6,810.42	10	6,453.07	2	6,217.01	5	5,931.06	7
7,174.91	10*d*	6,799.27	7	6,450.37	25	6,212.45	2	5,930.59	5
7,172.91	25	6,797.67	2	6,445.87	12	6,208.37	8	5,925.91	5*b*
7,152.71	2	6,790.07	5	6,444.61	10	6,200.32	3	5,922.39	3*b*
7,148.61	30	6,788.98	18	6,443.88	7*b*	6,194.94	3	5,918.94	15
7,135.22	4	6,787.59	1	6,440.42	3*b*	6,194.39	2	5,916.51	9
7,125.72	20	6,776.68	1	6,437.33	6	6,193.11	7	5,912.79	4*b*
7,121.27	10	6,774.22	15*c*	6,434.54	3	6,189.67	7	5,907.68	2*b*
7,118.06	3	6,771.71	20	6,430.78	30	6,179.04	4	5,904.34	5
7,117.51	12*b*	6,770.33	4	6,428.62	15*b*	6,170.85	4	5,901.90	12
7,116.07	4*b*	6,755.82	5	6,426.72	4	6,170.47	6	5,897.93	4
7,108.06	5	6,754.88	10	6,425.44	3	6,167.38	2	5,895.19	5*b*
7,093.00	10	6,740.74	18	6,418.48	2	6,165.61	1	5,892.45	3
7,092.14	3*b*	6,726.88	1	6,417.99	2*v*	6,160.05	1	5,888.49	4
7,091.35	2	6,714.44	3	6,392.18	8	6,158.84	8	5,886.46	3
7,085.39	10	6,709.36	10	6,389.45	20	6,154.49	15	5,882.29	12
7,081.35	8*b*	6,706.42	6	6,387.98	3	6,152.52	8	5,881.40	3
7,074.64	4	6,705.94	4	6,379.07	7	6,147.06	4*b*	5,877.36	20
7,049.87	3*b*	6,702.96	4	6,373.06	10	6,144.60	10*c*, *l*	5,872.03	3
7,039.06	12	6,699.05	1	6,369.04	3	6,141.19	3	5,866.58	8
7,036.56	3	6,693.60	7	6,364.92	5	6,140.08	8	5,865.85	7
7,031.50	6	6,691.97	1	6,364.06	2	6,138.11	2	5,861.43	3

TABLE 1.—*Wave lengths in the first spectrum of tantalum,* Ta I—Continued

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
5, 859. 73	1	5, 605. 51	7*b*	5, 342. 24	12	5, 069. 90	7	4, 758. 05	5*c*
5, 857. 90	2	5, 598. 76	7	5, 341. 06	35*c*	5, 067. 86	25	4, 756. 50	10
5, 857. 05	2	5, 592. 66	2	5, 336. 12	15	5, 064. 58	3	4, 754. 10	4*b*
5, 854. 92	2	5, 589. 04	1*n*	5, 328. 38	20*c*	5, 058. 69	5*b*	4, 745. 92	5
5, 853. 86	3	5, 584. 02	15*c*	5, 317. 32	3	5, 044. 86	3	4, 740. 14	10*c*
5, 849. 81	12*c*	5, 581. 39	4	5, 310. 92	2	5, 044. 40	7	4, 739. 44	3
5, 848. 85	5*b*	5, 577. 21	3	5, 295. 00	20	5, 043. 32	25	4, 738. 34	4
5, 847. 95	2	5, 566. 99	4*n*	5, 293. 40	6	5, 041. 85	5	4, 730. 11	8
5, 843. 93	12	5, 555. 80	1*b*	5, 287. 07	3	5, 039. 85	2	4, 722. 88	8
5, 842. 85	3	5, 549. 32	3	5, 281. 05	10	5, 037. 65	30	4, 706. 10	8+Cb?
5, 837. 29	2	5, 548. 32	10*b*	5, 279. 80	12	5, 037. 33	30*c*	4, 701. 31	7
5, 836. 64	2	5, 545. 20	8*c*	5, 275. 01	12	5, 017. 06	7	4, 693. 35	7
5, 835. 86	3	5, 536. 76	5*b*	5, 273. 25	4	5, 012. 54	25	4, 691. 91	20*c*
5, 828. 17	3	5, 530. 37	5*b*	5, 261. 53	3*b*	4, 998. 15	3	4, 688. 84	4
5, 825. 11	4*b*	5, 528. 36	7*b*	5, 260. 41	4	4, 993. 27	3	4, 685. 27	5
5, 824. 35	2	5, 523. 99	6*b*	5, 252. 13	3*b*	4, 977. 82	4	4, 684. 88	8
5, 820. 74	2	5, 521. 15	5	5, 247. 72	3*b*	4, 976. 19	7	4, 684. 22	3
5, 816. 51	8	5, 520. 21	2*n*?	5, 244. 77	4*b*	4, 969. 73	15*c*	4, 681. 88	15
5, 811. 10	20*d*?	5, 518. 91	30*c*	5, 235. 39	12*c*	4, 968. 52	7	4, 679. 46	3*n*
5, 799. 47	4	5, 517. 69	4*b*	5, 233. 43	5	4, 958. 09	8	4, 678. 01	5
5, 797. 70	4*b*	5, 516. 24	5*b*	5, 230. 80	15	4, 938. 86	3*b*	4, 669. 15	12
5, 793. 76	4	5, 513. 52	6*b*	5, 218. 67	25	4, 937. 63	15	4, 661. 10	12*c*
5, 792. 50	4	5, 505. 67	10	5, 218. 44	20	4, 936. 41	30	4, 651. 92	3*n*
5, 783. 27	5	5, 503. 05	2	5, 215. 35	2	4, 933. 50	6	4, 640. 77	6*b*
5, 780. 70	18	5, 500. 69	15	5, 212. 75	35*c*	4, 931. 57	3	4, 633. 05	8
5, 780. 01	10	5, 494. 81	18	5, 206. 55	2	4, 926. 02	35	4, 622. 96	5
5, 779. 31	4*b*	5, 490. 13	20	5, 206. 24	3	4, 924. 96	10	4, 621. 81	4
5, 776. 76	20	5, 486. 77	2	5, 193. 99	3*b*	4, 923. 47	15*c*	4, 619. 52	15
5, 771. 94	8	5, 485. 44	1*n*?	5, 188. 92	4	4, 922. 59	3*b*	4, 604. 86	4*c*?
5, 767. 90	15*c*	5, 481. 13	15+Cb?	5, 180. 93	7*c*	4, 921. 29	25	4, 602. 19	7*c*
5, 766. 55	12	5, 475. 57	25	5, 173. 11	7*b*	4, 920. 88	10	4, 601. 42	7
5, 765. 69	1	5, 472. 22	7	5, 171. 64	5*b*	4, 920. 13	35*c*	4, 583. 18	4*b*
5, 761. 59	8	5, 471. 54	10	5, 166. 79	12	4, 918. 85	3	4, 580. 70	7
5, 755. 80	12	5, 461. 31	25	5, 163. 64	15	4, 917. 20	5	4, 576. 60	4
5, 755. 04	2	5, 458. 43	10	5, 161. 82	18*c*	4, 914. 97	10	4, 574. 32	15
5, 754. 54	1	5, 456. 60	3	5, 156. 57	20	4, 911. 38	7	4, 573. 32	8
5, 751. 79	2	5, 454. 46	3	5, 156. 33	20	4, 907. 72	12	4, 571. 98	4
5, 749. 80	2	5, 446. 22	5	5, 153. 42	15	4, 904. 58	20	4, 566. 85	4
5, 746. 68	10	5, 438. 34	3	5, 150. 87	7	4, 901. 57	3*n*?	4, 565. 86	10
5, 740. 08	3	5, 435. 27	30	5, 148. 76	7	4, 883. 94	8	4, 556. 35	10*c*
5, 735. 16	2	5, 433. 00	8*b*	5, 147. 94	4	4, 881. 94	5	4, 553. 70	6*b*
5, 733. 51	4	5, 431. 65	10	5, 145. 18	2	4, 881. 51	2	4, 551. 96	12*c*
5, 730. 51	4*b*	5, 419. 19	30*c*	5, 143. 70	20	4, 879. 13	4	4, 547. 17	4
5, 727. 72	4*b*	5, 418. 01	6	5, 141. 83	4	4, 871. 68	5*b*	4, 530. 80	12
5, 724. 41	3	5, 413. 47	20*c*	5, 141. 63	30*c*	4, 864. 65	3	4, 527. 50	8
5, 722. 78	4*b*	5, 410. 55	10	5, 139. 03	2	4, 864. 34	2	4, 521. 71	2
5, 716. 53	8*b*	5, 408. 78	15	5, 136. 47	30*c*	4, 862. 50	3	4, 521. 09	10*b*
5, 715. 25	12	5, 405. 80	6*b*	5, 135. 89	4	4, 861. 04	3	4, 511. 48	7
5, 706. 30	15*c*	5, 404. 95	35*b*	5, 133. 88	2	4, 852. 67	3	4, 510. 97	40*f*,?
5, 704. 31	10	5, 403. 53	5	5, 132. 32	7	4, 852. 16	7	4, 509. 28	6
5, 699. 24	18	5, 402. 51	40*b*	5, 132. 10	12	4, 846. 80	4*d*?	4, 496. 50	6
5, 697. 95	1	5, 397. 54	15	5, 130. 52	4	4, 846. 43	8	4, 494. 98	3
5, 688. 25	15	5, 395. 96	20*c*	5, 126. 66	3*b*	4, 843. 79	3	4, 480. 92	7
5, 685. 50	2	5, 389. 30	25*c*	5, 122. 31	5	4, 832. 16	7	4, 473. 53	10
5, 680. 04	1	5, 388. 48	15	5, 117. 23	12	4, 825. 42	8	4, 462. 36	3
5, 667. 71	1	5, 385. 79	3	5, 115. 84	35	4, 821. 93	4	4, 459. 79	12
5, 664. 90	25+Cb?	5, 385. 25	3*n*?	5, 109. 78	12	4, 819. 52	9	4, 450. 73	10
5, 659. 28	2	5, 383. 88	3	5, 109. 37	12*c*	4, 815. 12	5	4, 441. 76	{12*b*, {+Cb?
5, 654. 86	2*b*	5, 379. 65	4	5, 098. 37	7	4, 812. 74	10		
5, 651. 59	2	5, 373. 00	8	5, 091. 64	4	4, 810. 35	4*n*	4, 441. 05	12
								4, 432. 97	7
5, 645. 92	20*d*?	5, 365. 92	8	5, 090. 71	25	4, 789. 27	2		
5, 640. 19	12	5, 354. 67	30*c*	5, 087. 37	20	4, 786. 65	6	4, 431. 09	4
5, 635. 71	10	5, 349. 58	25	5, 082. 26	15	4, 780. 94	8	4, 430. 96	5
5, 620. 69	15*c*	5, 349. 08	25*c*	5, 076. 38	18	4, 768. 99	10	4, 430. 40	12
5, 617. 73	5	5, 348. 09	2	5, 072. 45	3	4, 758. 90	3	4, 424. 97	3
								4, 419. 56	5

TABLE 1.—*Wave lengths in the first spectrum of tantalum*, Ta I—Continued

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
4,415.74	12	4,063.41	3	3,885.20	8	3,732.74	3	3,625.23	8
4,402.49	20c	4,062.80	4	3,879.43	5	3,731.02	10	3,624.10	4*b*
4,398.45	10	4,062.58	3	3,876.56	5	3,728.84	4	3,623.41	2
4,386.07	10	4,061.39	10c	3,875.21	4*b*	3,728.11	4	3,620.01	2
4,378.82	10	4,058.47	4	3,872.73	4	3,727.46	3	3,617.31	3
4,375.15	4	4,058.14	3*b*	3,870.64	4*b*	3,725.58	2	3,616.01	4
4,374.21	3	4,055.38	4*b*	3,866.70	3	3,725.03	2	3,612.82	2
4,372.80	4	4,054.40	4*b*	3,866.47	5	3,723.09	4	3,612.37	2
4,369.36	4	4,041.80	4	3,861.06	4	3,720.62	1	3,611.13	5
4,364.83	4	4,041.37	3	3,859.82	8	3,719.40	2	3,609.33	4
4,360.81	7c	4,041.05	8	3,858.59	7*b*	3,718.45	3	3,609.17	5
4,358.65	4	4,040.86	10	3,853.58	4	3,718.09	3	3,608.76	6
4,355.13	10c	4,039.62	4	3,851.43	3	3,714.89	3	3,607.41	15
4,351.01	4	4,035.90	7	3,849.74	4	3,714.35	2	3,604.97	4
4,344.32	6	4,033.07	8	3,849.44	6	3,711.15	3	3,600.70	4
4,336.29	2	4,031.95	3	3,848.05	10	3,710.79	4	3,598.81	3
4,329.59	5	4,030.67	4	3,846.62	5	3,709.66	2	3,598.06	3
4,322.70	4	4,029.94	10	3,844.04	5	3,706.59	2	3,596.86	4
4,318.82	5	4,026.94	12	3,842.88	7	3,706.31	2	3,595.64	7
4,314.54	5	4,015.23	5	3,842.34	5	3,706.08	3	3,592.49	4
4,302.97	15c	4,014.63	3*b*	3,839.42	4	3,705.17	3	3,592.14	3
4,286.40	6c	4,013.54	3	3,839.04	10	3,704.24	3	3,589.97	3
4,280.48	5	4,013.18	4	3,836.62	8	3,703.27	3	3,586.29	7
4,279.07	10	4,012.10	5	3,833.76	15	3,701.33	4	3,584.50	7
4,271.52	7*b*	4,007.22	4	3,832.28	4	3,700.27	3	3,584.21	7
4,268.27	10c	4,006.83	10	3,828.95	10	3,699.99	3	3,580.90	2
4,245.36	10	4,006.24	4*n*	3,826.85	10	3,695.39	5	3,580.04	2
4,244.00	5	4,003.70	6	3,826.18	6	3,693.05	6	3,579.08	5
4,228.63	10	3,999.27	15	3,823.60	12	3,689.74	5	3,578.77	2
4,224.62	4	3,996.16	20c	3,820.75	5	3,686.82	4	3,577.78	3
4,206.40	15	3,995.28	3	3,819.72	5	3,686.19	5	3,576.24	2
4,205.88	20c	3,990.39	4	3,812.85	4*b*	3,685.89	2	3,573.43	5*b*
4,201.97	4*b*	3,988.70	8	3,812.32	4*b*	3,684.97	3*b*	3,571.85	6
4,193.10	4	3,984.97	4*b*	3,809.70	4	3,684.31	3	3,571.15	4
4,191.27	4*b*	3,984.26	3	3,809.26	3	3,683.05	4	3,570.74	4*b*
4,191.18	7	3,983.82	4	3,807.74	3	3,681.26	4	3,570.32	4
4,181.15	10c	3,981.95	8	3,802.02	4*b*	3,681.05	3	3,569.19	3
4,177.91	7	3,981.01	4	3,801.79	4	3,676.88	3	3,567.35	4
4,177.00	4	3,979.27	6c	3,801.14	4	3,675.49	3	3,566.73	7
4,175.20	40c	3,970.10	15	3,800.00	4	3,675.13	4	3,566.01	3
4,161.00	5	3,968.16	4*b*	3,797.41	4	3,674.83	5	3,564.80	5
4,159.98	3	3,959.72	4	3,792.03	9	3,666.88	3	3,557.95	5*d*?
4,154.41	7*n*?	3,956.58	5	3,788.76	5	3,666.10	3	3,556.55	2
4,147.90	15	3,954.30	4*b*	3,785.26	4	3,665.35	3	3,555.71	4
4,136.21	15	3,952.16	5*b*	3,784.26	15c	3,663.83	3	3,553.43	5
4,129.37	30c	3,942.22	3	3,783.78	4	3,663.10	3	3,549.07	5
4,127.88	8	3,937.85	5	3,782.30	4	3,662.34	5	3,540.82	4
4,123.65	3	3,930.93	7	3,780.16	4	3,661.68	5	3,537.55	4
4,123.17	10c	3,930.23	4	3,779.10	4*b*	3,658.78	6*b*	3,536.30	5
4,118.06	3	3,925.26	4	3,777.11	7*b*	3,657.49	5	3,532.22	4
4,114.78	4	3,922.93	9	3,770.92	6	3,657.28	5	3,531.59	6
4,105.03	10	3,922.77	10	3,760.20	4	3,656.90	4	3,528.63	5
4,104.24	5	3,922.42	4*b*	3,759.76	5	3,656.34	2	3,527.08	5
4,097.19	4	3,918.52	10	3,757.74	4	3,656.05	3	3,517.45	3
4,092.10	3*n*?	3,912.43	4	3,755.09	6	3,655.94	3	3,514.39	3
4,091.65	3	3,912.13	4	3,754.52	5	3,655.65	2	3,513.62	5
4,091.26	7*b*	3,909.33	4	3,747.25	4*n*	3,653.81	4	3,512.82	3*b*
4,085.79	5	3,905.28	4*b*	3,746.38	8	3,653.40	5	3,511.04	10
4,081.78	3	3,898.76	4	3,743.67	3	3,652.42	4	3,507.33	2
4,079.19	8	3,898.15	4	3,742.67	3	3,648.00	4	3,506.90	3
4,077.72	5	3,896.43	4*n*	3,742.09	3	3,642.06	20	3,505.19	7
4,073.00	4	3,894.67	4	3,741.27	2	3,633.75	5	3,504.96	7
4,067.90	20c	3,893.03	3	3,738.25	3	3,627.01	5	3,503.87	8
4,067.23	15	3,890.70	3	3,737.96	2	3,626.61	10	3,502.88	5
4,064.63	15	3,890.50	3	3,736.77	10	3,625.68	4*n*	3,502.50	5

TABLE 1.—*Wave lengths in the first spectrum of tantalum,* Ta I—Continued

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
3,501.96	4*d*?	3,405.69	1	3,311.16	20*c*	3,239.98	5*c*	3,154.50	3
3,497.85	10	3,404.16	3	3,309.80	5	3,237.86	5	3,153.93	2
3,493.44	4*c*	3,401.83	3	3,308.89	1	3,236.40	4	3,153.08	4*b*
3,490.95	5	3,398.34	9	3,308.56	2	3,235.87	2	3,152.54	3
3,489.16	3	3,397.42	2	3,307.10	3	3,234.69	5	3,152.01	2
3,488.86	4	3,395.40	1	3,305.36	3	3,232.28	4	3,150.84	5
3,488.55	2	3,393.43	1	3,305.14	3	3,231.67	3	3,149.77	3
3,487.39	3	3,388.83	4	3,304.39	5	3,230.87	10*c*	3,148.04	5
3,486.69	4	3,387.46	4	3,304.05	4	3,229.87	5*c*	3,147.39	5*c*
3,484.63	5	3,387.23	2	3,302.78	4	3,229.23	10*c*	3,146.77	3
3,484.24	2	3,385.05	10	3,302.32	2*b*	3,227.32	6	3,141.01	2
3,480.51	10*d*?	3,383.84	3	3,301.91	4	3,226.86	5	3,138.50	4*b*
3,479.44	3	3,383.16	1	3,299.78	6	3,226.32	3	3,138.32	3
3,477.63	2	3,381.97	3	3,299.28	3	3,223.84	10	3,136.59	2
3,477.44	4	3,380.64	4	3,297.19	2*b*	3,221.32	7	3,136.30	2
3,477.23	3	3,379.95	3*b*	3,295.33	7*d*?	3,220.06	3*c*	3,135.88	5
3,473.90	5	3,379.51	5	3,294.74	2	3,219.60	6*c*	3,133.55	4
3,473.33	4	3,378.20	2	3,293.94	5	3,217.98	3*b*	3,132.65	7
3,472.84	4	3,377.78	3	3,292.50	5	3,216.92	7*d*?	3,131.24	2
3,472.53	5	3,376.49	4	3,291.91	4, Cb?	3,216.64	2	3,130.60	7*d*
3,466.86	3	3,376.05	5	3,291.39	3*b*	3,215.99	3	3,130.31	2
3,465.51	2	3,373.72	2	3,289.86	3	3,209.85	3	3,129.96	6
3,463.93	4	3,371.54	10	3,288.48	3	3,208.64	3	3,129.56	6
3,462.87	3	3,369.28	5	3,287.28	3	3,208.21	3	3,129.15	4
3,462.19	2	3,366.66	5	3,286.44	1	3,207.86	6	3,124.97	6
3,460.12	3	3,365.03	3	3,284.63	3	3,206.79	3	3,121.54	2
3,458.53	2	3,364.12	3	3,283.83	2	3,206.38	7	3,120.92	4
3,456.07	2	3,362.53	4	3,282.55	1*b*	3,205.48	5*b*	3,119.62	4
3,453.36	2	3,361.66	6	3,280.88	6	3,203.76	4*c*	3,117.45	6
3,452.98	4	3,358.99	4	3,280.27	2	3,201.97	4	3,115.87	5*d*?
3,450.42	3	3,358.47	10	3,279.28	6	3,198.67	8*c*	3,113.91	6*c*
3,448.92	4	3,357.32	2	3,278.33	2	3,196.37	4	3,110.11	4
3,447.30	5	3,356.64	4*d*?	3,275.93	4*c*	3,192.24	8*c*	3,109.34	2
3,445.93	4	3,356.03	3	3,275.68	7	3,189.70	4*d*?	3,107.81	3
3,445.51	3	3,355.59	3	3,274.93	10*c*	3,189.09	2	3,107.22	5
3,445.10	4	3,355.32	2	3,274.47	3	3,188.47	3	3,105.15	2
3,444.69	4	3,353.91	1	3,273.14	4	3,184.56	7	3,104.43	4
3,444.08	4	3,351.86	3*b*	3,272.62	2	3,182.57	6	3,104.18	2
3,441.56	2	3,351.51	6	3,271.19	2*b*	3,181.70	7*d*?	3,103.26	8
3,440.25	5	3,350.98	5	3,269.16	5	3,180.95	10*d*?	3,101.73	4
3,437.37	2	3,347.04	2	3,267.56	2*b*	3,179.54	4	3,101.43	2
3,437.08	2	3,345.08	3	3,266.87	3*c*	3,178.23	6*c*	3,096.11	3
3,436.01	7*c*	3,344.39	2*b*	3,265.34	2	3,177.93	4	3,095.40	7
3,434.50	5	3,343.44	4	3,264.10	3	3,176.30	7	3,093.88	6
3,430.92	8	3,339.91	7	3,263.77	4	3,174.38	2	3,093.00	4
3,429.33	2*n*	3,339.52	2	3,263.02	2	3,173.58	8	3,092.46	6
3,426.74	4	3,338.50	5	3,260.20	6	3,173.46	5	3,092.07	4
3,426.19	3	3,337.80	6	3,259.89	5	3,172.87	6*b*	3,089.92	2
3,424.44	5	3,337.50	3*b*	3,259.64	4	3,172.25	2	3,087.52	5
3,423.03	1	3,336.36	2	3,258.24	3*d*?	3,170.98	1	3,086.65	1
3,421.81	2	3,334.75	3	3,257.84	2	3,170.30	8*c*	3,085.55	6
3,421.21	2	3,333.09	3	3,256.78	4	3,168.19	3	3,084.53	3
3,419.74	5	3,332.81	4	3,255.69	2	3,167.53	5	3,082.46	5
3,419.53	4	3,332.41	5	3,253.81	2	3,166.38	4	3,081.85	10
3,418.32	3	3,331.48	2*b*	3,253.34	2	3,163.82	5	3,079.96	10
3,417.03	4	3,331.02	10*c*	3,251.92	3	3,163.55	4	3,079.30	5
3,415.88	4	3,329.55	3	3,250.36	5	3,163.13	5	3,078.24	8
3,415.28	4	3,328.93	3	3,250.03	2	3,162.73	5	3,077.24	15*d*?
3,414.14	10	3,328.29	3*d*?	3,248.53	6	3,161.85	2	3,076.54	4
3,413.64	3	3,325.74	4	3,246.90	3	3,161.43	3	3,076.39	7
3,412.92	5	3,324.86	2	3,245.29	4	3,160.81	1	3,076.09	3
3,411.71	4	3,319.47	4	3,243.38	3	3,159.04	5	3,075.31	6
3,410.77	2*b*	3,318.87	12*c*	3,242.84	8	3,157.96	4	3,073.39	7
3,406.96	8	3,318.55	5	3,242.57	3	3,155.51	4	3,072.34	7*b*
3,406.64	8	3,317.93	10*c*	3,242.05	8	3,154.71	2	3,072.08	2

TABLE 1.—*Wave lengths in the first spectrum of tantalum*, Ta I—Continued

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
3,070.54	5	2,985.05	2	2,915.49	25	2,850.97	25	2,789.33	3
3,069.21	20c	2,984.35	10	2,915.33	20	2,850.48	20	2,788.31	12
3,066.76	4	2,983.99	2	2,914.94	8	2,849.82	18	2,787.69	50
3,063.87	4	2,981.96	5	2,914.12	20	2,849.53	3	2,787.03	4
3,063.56	18r	2,981.18	7	2,913.32	7	2,848.52	12	2,783.69	10
3,061.98	2	2,980.76	7	2,907.77	5	2,848.03	15	2,782.76	3
3,061.81	4	2,980.32	2	2,906.48	2	2,847.28	6	2,781.79	15
3,060.27	15	2,979.57	2	2,906.17	2	2,846.75	12	2,781.37	25
3,058.65	15d?	2,978.74	20	2,905.73	10	2,845.82	8	2,780.64	2
3,057.12	5	2,977.73	4b	2,904.42	8	2,845.46	3	2,780.20	10
3,054.80	5	2,977.55	6	2,904.07	15	2,845.34	20	2,779.72	20+Cb?
3,051.91	6	2,976.76	10	2,902.61	8	2,844.76	10r	2,779.34	4
3,051.21	2	2,976.12	8	2,902.05	25	2,844.23	12r	2,779.11	35
3,050.98	3	2,975.54	20	2,901.64	3	2,842.80	15	2,775.90	20r
3,050.11	8	2,971.96	7	2,901.04	10	2,842.34	3	2,774.88	10
3,049.56	18	2,969.88	10	2,900.34	20r	2,839.76	7	2,772.59	4
3,048.87	12	2,969.47	20	2,899.02	10	2,837.93	12	2,770.76	10
3,048.31	5	2,967.84	2	2,898.41	10	2,836.61	12	2,768.90	4
3,045.95	15c	2,967.41	2	2,896.41	15W?	2,836.25	5	2,768.31	5
3,043.94	20	2,965.54	20r	2,895.08	12	2,834.41	15b	2,766.88	3
3,041.53	2	2,964.80	3	2,894.15	12	2,833.63	20	2,766.13	6
3,040.98	8	2,963.91	10	2,893.79	5	2,830.02	4	2,765.27	3
3,038.91	3	2,963.32	35	2,893.20	2	2,827.14	15b	2,764.77	6
3,036.28	6	2,963.06	6	2,892.87	2	2,826.42	10	2,764.27	4
3,035.82	4	2,962.09	2	2,892.25	2	2,826.19	12	2,761.52	5
3,034.98	2	2,961.39	3	2,892.00	10	2,825.05	4	2,761.16	2
3,033.40	3	2,958.13	4	2,891.84	30	2,824.81	8	2,760.69	3
3,030.28	8	2,957.58	12	2,891.02	15	2,824.05	3	2,758.31	20r
3,029.53	7	2,956.06	2	2,890.53	2	2,822.37	2	2,757.98	2
3,028.78	10	2,953.55	20	2,890.06	3	2,821.98	15	2,757.12	4
3,027.48	20c	2,951.92	30	2,889.37	15	2,821.17	6	2,752.29	10
3,025.17	10	2,948.51	3	2,888.13	2	2,819.38	8	2,751.04	4
3,024.28	5	2,947.81	10	2,886.63	7	2,818.74	5	2,750.55	4
3,022.77	4	2,947.39	3	2,885.71	2	2,817.50	10	2,748.77	20
3,022.28	7	2,947.18	2	2,884.96	3	2,816.16	2	2,747.84	7
3,021.55	2	2,946.91	25	2,883.88	7	2,815.79	2	2,747.25	12
3,019.66	10	2,946.27	5	2,882.33	15	2,815.11	10	2,746.68	8
3,019.09	8	2,943.77	8	2,881.21	6	2,814.80	10	2,745.56	4
3,016.36	10	2,942.13	20	2,880.00	20	2,810.91	25	2,743.58	10
3,012.84	2	2,940.21	25	2,879.73	10	2,810.06	2	2,742.91	8
3,011.88	15	2,940.02	20b	2,878.94	5	2,808.07	4	2,741.37	8
3,011.11	20	2,939.29	15	2,878.19	8	2,806.59	25	2,741.16	12
3,007.53	5	2,938.57	2	2,876.13	20b	2,806.29	20	2,740.18	8
3,006.54	8	2,938.44	10	2,874.93	5	2,805.08	7	2,737.09	4
3,005.04	4	2,937.49	2	2,874.75	2	2,804.75	10	2,736.24	20
3,004.92	12	2,937.30	2	2,874.51	6	2,804.02	7	2,734.52	5
3,004.14	6	2,935.95	8	2,874.14	12	2,802.71	20	2,733.68	3
3,001.53	10	2,935.58	4	2,873.56	15	2,802.50	5	2,732.91	10
2,997.02	4	2,935.15	4	2,873.34	15	2,802.06	30	2,732.05	12
2,996.86	4	2,934.85	10	2,871.40	25	2,800.82	2	2,730.32	3
2,996.00	3	2,934.50	2	2,869.52	5	2,800.56	15	2,729.50	2
2,993.60	4	2,933.54	30	2,869.20	2	2,800.33	2	2,729.27	3
2,993.13	8	2,932.67	25b	2,868.62	25	2,799.39	4	2,728.32	2
2,992.38	5	2,930.99	12	2,866.67	5	2,798.90	2	2,727.77	15
2,991.22	10	2,926.46	10	2,866.12	15	2,798.40	15r	2,726.32	8
2,990.73	4	2,925.65	10	2,865.09	2	2,796.55	15	2,725.07	6
2,989.88	3	2,925.21	30b	2,864.72	2	2,796.33	25	2,724.34	12
2,989.48	20	2,924.78	8	2,864.48	15	2,793.28	2	2,723.86	15
2,989.04	7	2,923.52	3	2,864.26	6	2,792.66	10b	2,723.26	8
2,988.56	15	2,922.41	4	2,862.36	4	2,791.67	20	2,722.89	2
2,987.16	4	2,920.30	5	2,861.98	20	2,791.16	3	2,722.32	5
2,986.40	6	2,917.11	8b	2,861.76	3	2,790.72	25	2,721.83	10
2,986.17	2	2,916.82	7	2,857.29	15	2,790.46	10	2,720.74	12
2,985.93	2d?	2,916.32	4	2,854.16	4	2,789.77	20	2,718.37	15
2,985.69	3	2,916.04	2	2,852.94	10	2,789.53	2	2,717.18	15

TABLE 1.—*Wave lengths in the first spectrum of tantalum,* Ta I—Continued

λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes	λ_{air}A	Intensity and notes
2,715.87	3	2,660.04	2	2,601.30	3	2,550.78	5	2,471.38	5
2,714.66	18r	2,659.66	12	2,601.05	15	2,550.57	4	2,471.24	3
2,711.92	2	2,657.69	4	2,600.14	10	2,550.46	5	2,469.76	4
2,710.12	20r	2,657.41	2	2,599.40	15+Fe?	2,549.39	10	2,468.07	4
2,708.35	6	2,657.30	10	2,599.10	2	2,547.23	2	2,465.38	2
2,708.14	5	2,656.61	30r	2,598.75	10	2,546.81	10	2,465.27	7
2,707.83	8	2,656.35	3	2,597.50	5	2,544.82	5	2,461.25	3
2,707.65	3	2,656.06	8	2,596.60	5	2,544.27	5	2,460.56	6
2,707.51	2	2,655.68	10	2,596.12	10	2,543.29	1	2,459.58	5
2,706.91	7	2,654.00	10	2,595.26	15r	2,542.23	5	2,458.69	5
2,706.68	12	2,653.27	50r	2,594.73	2	2,541.95	6	2,454.48	7
2,706.14	4	2,652.32	12	2,594.55	2	2,541.43	4	2,454.22	7
2,705.77	2	2,651.49	4	2,593.67	18	2,539.99	2	2,453.25	2
2,704.30	15	2,650.28	18	2,593.09	15	2,539.71	4	2,450.92	3
2,703.53	6	2,650.02	15	2,592.43	8	2,536.66	2	2,449.27	1
2,703.05	12	2,649.76	1	2,592.20	5	2,536.20	5	2,449.10	1
2,702.21	8r	2,648.71	3	2,590.94	10	2,535.97	8	2,447.94	2
2,701.60	10	2,648.23	1	2,590.49	3	2,535.60	8	2,443.93	5
2,700.68	10	2,647.47	30r	2,589.27	2	2,534.98	10	2,442.39	8
2,700.58	5	2,646.36	20r	2,589.14	2	2,534.48	8b	2,440.95	3
2,700.30	2	2,646.21	25	2,588.54	8	2,534.17	2	2,439.90	5
2,700.15	3	2,643.88	15	2,587.25	7b	2,533.01	10	2,437.06	6
2,698.29	20	2,643.24	7	2,585.62	10	2,531.51	4	2,434.72	3
2,696.80	15	2,642.24	10	2,584.90	3	2,531.29	10	2,433.78	1
2,694.75	12	2,641.92	1	2,584.69	10	2,530.97	3	2,433.15	4
2,693.93	3	2,641.06	3	2,582.24	3	2,530.87	2	2,432.21	2
2,693.50	10	2,640.92	4	2,581.19	2	2,528.96	5	2,431.65	7
2,693.34	15	2,638.27	5	2,580.84	2	2,526.66	10	2,431.41	2
2,692.39	18	2,636.90	30r	2,580.15	12	2,526.34	10	2,430.07	2
2,691.31	18r	2,636.67	25r	2,579.62	12	2,525.80	3	2,429.34	5
2,690.54	10	2,636.36	8	2,578.74	4	2,525.31	5	2,428.98	4
2,690.25	2	2,635.93	8	2,578.39	4	2,522.32	1	2,427.63	18
2,689.53	6	2,634.71	2	2,577.97	4	2,520.75	2	2,426.58	4
2,687.16	4	2,634.11	4	2,577.78	10r	2,520.31	5	2,422.81	4
2,686.95	2	2,629.98	6	2,575.47	15r	2,519.78	12	2,422.08	4
2,686.29	15	2,628.49	2	2,574.38	15	2,518.77	3	2,421.03	5
2,685.46	3	2,627.43	5	2,573.80	15	2,516.70	4	2,419.72	4
2,684.27	18r	2,627.06	5	2,573.54	18	2,515.15	5	2,417.69	5
2,681.88	12	2,626.07	3	2,572.10	3	2,512.64	12	2,416.56	2
2,681.64	4	2,625.80	4	2,571.19	4	2,512.03	6	2,414.32	4
2,677.87	5	2,625.46	8	2,569.79	2	2,511.01	4	2,412.67	4
2,677.66	2	2,624.12	8	2,567.48	4	2,509.18	6	2,407.56	6
2,677.46	2	2,623.16	2	2,567.34	4	2,507.45	15	2,406.55	10
2,677.16	5	2,622.95	2	2,566.74	3	2,505.90	1	2,404.22	5
2,675.54	3	2,620.19	10	2,566.33	12	2,504.68	4b	2,403.98	5
2,674.48	10	2,617.63	10	2,565.78	5	2,504.45	20	2,401.71	6
2,673.58	10	2,616.48	5	2,565.41	4	2,501.51	2	2,399.16	3
2,673.29	6	2,615.66	12	2,565.21	4	2,500.74	2	2,398.98	3
2,672.34	6	2,615.48	10	2,563.87	5	2,498.76	4	2,398.25	4
2,671.93	10	2,615.26	10	2,563.71	10	2,498.59	2	2,397.85	4
2,671.63	12	2,614.16	2	2,563.34	8	2,496.96	3	2,396.31	8
2,671.28	2	2,612.38	2	2,562.76	2	2,496.65	5	2,391.13	5
2,671.01	5	2,611.48	6	2,562.40	3	2,494.90	2	2,390.86	2
2,669.07	3	2,611.36	12	2,562.10	10	2,492.75	2	2,387.17	2
2,668.62	20	2,610.28	2	2,561.95	2	2,491.58	3	2,385.74	6
2,668.06	15	2,610.14	10	2,560.68	15	2,488.39	3	2,385.34	4
2,667.76	5	2,609.00	12	2,559.43	25	2,488.20	3	2,380.18	3
2,667.15	6	2,608.63	15r	2,558.95	2	2,486.70	8+Fe?	2,380.00	5
2,665.94	10	2,608.22	8	2,558.59	4	2,484.96	10		
2,663.42	2	2,606.56	3	2,556.93	3	2,478.83	2	2,378.52	2
								2,375.86	5
2,662.61	3	2,605.82	4	2,555.07	10	2,478.22	8	2,371.85	2
2,662.10	12	2,605.33	10	2,552.32	2	2,476.33	2	2,368.46	2
2,661.88	18	2,603.83	10	2,551.35	8	2,474.62	10		
2,661.33	30r	2,602.38	12	2,551.20	8	2,472.62	1		
2,660.23	3	2,601.98	3	2,551.06	12	2,472.14	8		

In conclusion we desire to acknowledge our indebtedness to the various persons who have aided us in carrying forward the work described in this paper. To Dr. C. W. Balke we express our thanks for the gift of the rod of tantalum metal used for the arc and spark electrodes; to Dr. W. F. Meggers, of the Bureau staff, for making the underwater spark exposure; to Dr. B. H. Carroll, formerly of the Bureau staff, for making the Schumann plates; and to D. D. Laun, formerly of the Bureau staff, for assistance in the wave-length calculations.

WASHINGTON, D.C., February 21, 1934.

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RESEARCH PAPER RP672

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SOME OPTICAL AND CRYSTALLOGRAPHICAL PROPERTIES OF THE ALKALI ZINC URANYL ACETATES

By Herbert Insley and Francis W. Glaze

ABSTRACT

The optical properties and crystal form of the zinc uranyl acetates of sodium, lithium, and potassium were determined. The lithium and sodium zinc uranyl acetates belong to the monoclinic system and are isomorphous. They are capable of forming a series of solid solutions, as is evidenced by the homogeneity and the intermediate optical properties and X-ray pattern of a mixed sodium and lithium zinc uranyl acetate. The potassium zinc uranyl acetate belongs to the tetragonal system and differs from the lithium and sodium zinc uranyl acetates in optical properties and crystal form.

In studying the application of the Barber and Kolthoff method [1] for the quantitative determination of sodium to the analysis of glass,[2] a casual examination of the crystalline precipitate showed that the crystals were, in general, very well formed and were characterized by twinning. Barber and Kolthoff stated that part of the potassium and most of the lithium are precipitated with the sodium salt when they are present. Glaze has recently substantiated Barber and Kolthoff's statement that lithium cannot be separated from sodium, but has shown that potassium can be separated from sodium if proper precautions are taken.[3] Hence it seemed desirable to make a detailed study of the three salts to see if they can be readily distinguished by their optical properties.

The crystalline compounds used in this work were prepared as follows: One volume of a solution of cp alkali chloride was mixed with 10 volumes of the zinc uranyl acetate reagent [4] and stirred frequently during 30 minutes. The precipitate was filtered and washed free from the excess reagent with 95 percent alcohol and finally with ether.

The precipitate was dissolved in a minimum amount of distilled water and recrystallized by slowly concentrating the solution in a dessicator over sulphuric acid. In the case of the potassium salt a few drops of acetic acid were added to prevent hydrolysis.

Microscopic examination of the sodium and lithium salts showed them to be perfectly homogeneous and without visible impurity. Analyses of these two salts were made as follows: The uranium was converted to sulphate by fuming with sulphuric acid, reduced in a Jones reductor, oxidized to quadrivalent uranium with air and

[1] Jour. Am. Chem. Soc., vol. 50, pp. 1625-1631, 1928.
[2] F. W. Glaze, Jour Am. Cer. Soc., vol. 14, no. 6, pp. 450-453, 1931.
[3] B.S. Technical News Bulletin No. 94, p. 68, June 1933.
[4] Barber and Kolthoff, op. cit., p. 1626.

titrated with permanganate. The zinc was precipitated from a 0.008 *N* sulphuric acid solution by hydrogen sulphide. The precipitate was dissolved and reprecipitated until white in color, filtered, and ignited to the oxide. The alkali was determined as sulphate on a separate sample after removing the uranium and zinc as sulphides from an ammoniacal solution. On the lithium salt water was determined at 100 C and 3 mm pressure and the acetic acid was determined by distilling from a phosphoric acid solution and titrating with standard sodium hydroxide. The results of the analyses are given in table 1 together with the compositions calculated from the formulas (see footnote 4).

TABLE 1.—*Results of analyses*

Components	$NaZn(UO_2)_3(CH_3COO)_9.6H_2O$		$LiZn(UO_2)_3(CH_3COO)_9.6H_2O$	
	Found	Calculated	Found	Calculated
	Percent	*Percent*	*Percent*	*Percent*
UO_2	52.90	52.69	53.29	53.25
Zn	4.35	4.25	4.36	4.30
Na	1.47	1.495		
Li			.46	.456
$CH_3.COO$	[a]	34.54	34.77	34.90
H_2O	[b]	7.03	7.12	7.10

[a] Not determined.
[b] Not determined. See Barber and Kolthoff, op. cit., p. 1628.

The potassium salt contained a very small amount (estimated at less than 1 percent) of an unidentified crystalline impurity.

The indices of refraction of the crystals were determined by the usual microscopic immersion method using sodium light and a series of mixtures of petroleum oil and alpha monobromnaphthalene, the members of which differed in index by approximately 0.005. Immediately thereafter the indices of the liquids were measured with an Abbe refractometer. The temperatures at both the microscope and the refractometer were known within one degree centigrade. The optic axial angle of the sodium salt was measured with a condenser apertometer plate.

Diffraction patterns of the powdered crystals for purposes of comparison were made with a Coolidge X-ray tube with molybdenum target and zirconium oxide filter.

The sodium zinc uranyl acetate occurs as monoclinic crystals of tabular habit with the crystallographic *b* axis as the long dimension. Of the crystals studied the largest were about 0.08 mm long and 0.33 mm wide. Indices of refraction are:

$$\alpha_{Na} = 1.475 \pm .002$$

$$\gamma_{Na} = 1.480 \pm .002$$

The optical character is negative, the optic axial angle ($2V$) being about 25°.[5] The obtuse bisectrix γ is parallel to the crystallographic *b* axis. The form of the crystal and the optical orientation are shown

[5] The optical character and size of optic angle reported in the Technical News Bulletin, Bureau of Standards, November 1933, were incorrect.

in figure 1. The angular relations between faces and between optical and crystallographical directions as shown in the figure are those obtained by microscopic measurement and consequently are only approximate. Accurate determinations of the β index of refraction and of the optic axial angle could not be made, because of the difficulty of maintaining the crystals in the proper orientation for these measurements. Beautiful pseudo-rhombohedral forms produced by cyclic twinning are very abundant. The γ vibration direction makes an angle of about 31° with the trace of the twinning plane.

Individual crystals of lithium zinc uranyl acetate made by the method used were exceedingly rare. The few present evidently belonged to the monoclinic system and had faces similar to those of the sodium salt. All the other crystals observed were cyclic pseudo-rhombohedral twins with the same form and about the same optical orientation as the sodium salt. Indices of refraction are:

$$\alpha_{Na} = 1.495 \pm .002$$

$$\gamma_{Na} = 1.503 \pm .002$$

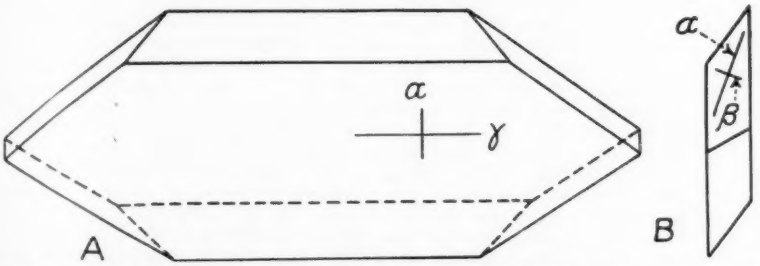

FIGURE 1.—*Diagrammatic representation of crystal of sodium zinc uranyl acetate, (A) with the tabular faces parallel to the plane of the paper and (B) with the crystallographic b axis normal to the plane of the paper. The approximate optical orientation is indicated.*

Satisfactory values for the β index of refraction and the optic axial angle were not obtainable.

The potassium zinc uranyl acetate consisted of well formed prismatic holohedral tetragonal crystals with simple combinations of prism (110) faces and first and second order pyramids. There is a perfect cleavage parallel to (110). Indices of refraction are:

$$\epsilon_{Na} = 1.487 \pm .002$$

$$\omega_{Na} = 1.477 \pm .002$$

The marked similarity in optical properties and in crystal form of the sodium and lithium salts suggests that they are isomorphous and may show complete solid miscibility. X-ray powder diffraction patterns of these two compounds confirm this supposition, the patterns showing complete similarity in arrangement and intensity of the lines, the interplanar spacings only being slightly different.

An X-ray photograph of the crystals made by adding the precipitating reagent to a solution containing equimolecular amounts of sodium and lithium chlorides gave a pattern in which the lines were intermediate in position between those of the pure sodium and the pure

lithium salts. Microscopically the crystals of the mixed salt appeared completely homogeneous and had indices of refraction between those of the pure end members. Evidently there is complete solid miscibility between the sodium and lithium salts.

The powder diffraction pattern of the potassium zinc uranyl acetate shows, as would be expected from the crystallographic data, little similarity in position, arrangement, or intensity of lines to those of the sodium and lithium salts.

Evidence obtained indicates that there is little prospect that separations of sodium and lithium by precipitation with zinc uranyl acetate can be made.

WASHINGTON, December 14, 1933.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP673

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THE CARBONIZATION PROCESS: A STUDY OF THE SYSTEM WOOL—SULPHURIC-ACID—WATER[1]

By Milton Harris[2]

ABSTRACT

The purpose of this study was to provide quantitative data on the system wool—sulphuric-acid—water under conditions similar to those in the soaking, drying, and baking of wool in the carbonization process as a basis for the effective study of mill problems relating to the process.

The amounts of sulphuric acid absorbed by wool from 0.1, 1, and 5 percent solutions at 22 C and from a 5 percent solution at 35 C and the rates of absorption are reported. It was found that wool treated with acid retains less moisture than similar wool treated only with water when dried in air of relative humidities 6, 30, 65, and 90 percent, the difference in the amount of water absorbed being greatest for the 30 and 65 percent relative humidities. When the dried wool is baked there is a critical moisture content for each concentration of acid in the wool above which the breaking strength of the wool decreases and the ammonia nitrogen content increases. The physical and chemical break-down increases with an increase in concentration of acid and with an increase in the temperature of baking. The deterioration takes place in the first few minutes of baking.

When acid-treated wool is stored in air of 65 percent relative humidity or less, there is no decrease in breaking strength, but there is chemical deterioration as evidenced by the ammonia nitrogen content which increases with time of storage. The higher the relative humidity of the atmosphere in which the wool is stored and the greater the concentration of acid in the wool the more rapid is the increase in ammonia nitrogen content.

That the deterioration of wool in baking is promoted by the presence of oxygen, moisture, and sulphuric acid is demonstrated in experiments in sealed tubes.

The nature of the system wool—sulphuric-acid—water is discussed. Mechanisms by which moisture and acid may be taken up and held by wool are suggested.

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I. INTRODUCTION

The object of the carbonization process is the removal of vegetable matter from wool. The wool is impregnated with a solution of sulphuric acid,[3] squeezed or centrifuged to remove the adhering acid

[1] The work reported here was made possible by a grant from the Textile Foundation, Incorporated, to the American Association of Textile Chemists and Colorists.

[2] Research Associate at the Bureau of Standards for the American Association of Textile Chemists and Colorists.

[3] Aluminum chloride and hydrochloric acid are sometimes used instead of sulphuric acid. These reagents are not considered in this paper.

liquor, dried at about 160 F, baked at about 250 F, and finally washed or neutralized. The control of the process to avoid damage to the wool must be considered one of its important phases. It is probable that many, if not all, of the troubles in the subsequent processing of wool that are attributable to faulty carbonization arise from incipient damage to the wool.

A considerable amount of acid is absorbed by wool in the carbonization process. A knowledge of the nature of the wool-acid combination and the effect of the variables concerned is obviously basic to the control of carbonization. It is of importance from the standpoint of subsequent processing of the wool fiber; for example, dyeing from acid solutions. The purpose of this research is to supply quantitative data on the system wool—sulphuric-acid—water as a basis for the effective study of mill problems relating to the carbonization process.

The variations in the carbonization process as practiced in industry make it difficult to attempt to set up any one laboratory procedure to cover all of the conditions. Moreover, it was evidently desirable to carry out the experiments under conditions that could be strictly controlled in order to obtain reproducible quantitative values. A large excess of acid over wool was used in the soaking bath and soaking was continued until equilibrium was reached, to insure uniform distribution of the acid in the fiber. Similarly, in drying and baking, the wool was well exposed to the surrounding atmosphere. The conditions of these experiments may be considered to be "ideal" rather than practical, but it is believed that the results have considerable practical significance.

II. MATERIAL AND METHODS

The material used for the experiments was worsted cloth, plain weave, weighing 8 ounces per square yard, mill-processed ready for dyeing. It was purified in the laboratory by successive extractions of 24 hours each with alcohol and ether and, finally, was soaked in water at 60 C for 30 minutes to remove adsorbed solvents.[4] After air drying, the cloth was cut warpwise into specimens measuring 3½ by 6 inches.

The breaking strength of the cloth was taken as a measure of its physical breakdown in the experiments. A pendulum type testing machine and the strip method were used. Specimens 6 inches long and 1 inch wide, cut warpwise of the cloth, were tested. All specimens were thoroughly conditioned and tested in a room maintained at a relative humidity of 65 percent and a temperature of 70 F. The average strength of from 3 to 5 specimens is reported.

The amount of wool protein in a specimen at any stage of processing was obtained by determining the total nitrogen by the Kjehldahl method. This value, multiplied by the factor 6.33 (obtained by dividing a known weight of the purified wool by its nitrogen content), gave the figure taken for the amount of wool protein.

The chemical breakdown of the fiber in the experiments was followed by analyzing specimens for ammonia nitrogen; that is, that portion of the nitrogen which is liberated when the wool is boiled in a saturated solution of magnesium oxide.

[4] R. T. Mease, Adsorption of alcohol by fibrous materials, Ind. & Eng. Chem. Analytical Edition, vol. 5, p. 317, 1933.

Experiments in which specimens were exposed to air of different relative humidities were carried out by suspending the specimens in desiccators containing suitable saturated salt solutions. The salts used and the relative humidities are indicated in table 1.

TABLE 1.—*Relative humidities over saturated solutions at 70 F.*

	Relative humidity
Sodium hydroxide (NaOH)	[a] 6
Phosphoric acid ($H_3PO_4.½\ H_2O$)	[a] 9
Sodium chloride, potassium nitrate, and sodium nitrate (NaCl, KNO_3 and $NaNO_3$)	[b] 30
Zinc sulphate ($ZnSO_4.7H_2O$)	[c] 90

[a] Obermiller, Die Einstellung von Luft, Zeit. Phys. Chem., vol. 109, p. 145, 1924.
[b] Bronsted, Kgl. Danske Videnskab. Selskab, Math., fys. Medd. vol. 1, p. 5, 1918.
[c] Sedgewick and Eubank, Jour. Chem. Soc. vol. 125, p. 2268, 1924.

The moisture content of the wool specimens was determined with the apparatus shown in figure 1. The specimen is placed in chamber *A*. The U-tube *B* is immersed in liquid air. The apparatus is then evacuated. The moisture from the specimen passes over into the U-tube where it freezes. It is then weighed directly. *D* is a cotton

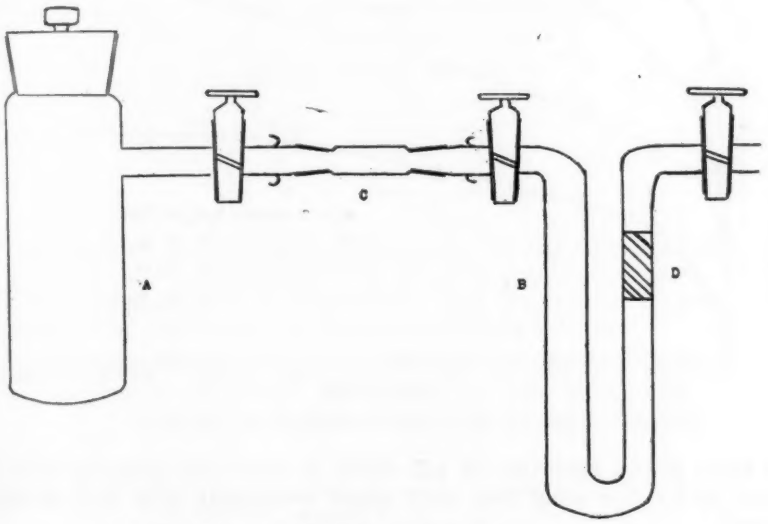

FIGURE 1.—*Apparatus for moisture determination.*

plug to prevent particles of ice from passing out of the tube. The rate of removal of moisture from wool by this method is slower than oven drying, equilibrium being reached in 24 to 30 hours. However, oven drying at temperatures above 100 C was found to be unsatisfactory, especially when much acid and water were present. Not only was it difficult to obtain a constant weight, but when the moisture and acid concentrations were high, the wool was degraded.

The amount of sulphuric acid in an acid-treated wool specimen was determined as barium sulphate by the following procedure. A 2-gram specimen of the wool was dissolved in 50 ml of an aqueous 5 percent solution of potassium hydroxide by warming on a steam bath.

The solution was made slightly acid with hydrochloric acid. Twenty ml of a 10 percent solution of barium chloride were added. The solution was filtered and the precipitate was washed with water until free from chloride and then ashed in an electric muffle furnace at 700 to 800 C.[5]

III. EXPERIMENTAL

1. DISTRIBUTION OF SULPHURIC ACID BETWEEN WOOL AND WATER IN THE SOAKING BATH

Two-gram specimens of wool were soaked in 50 ml portions of 0.1, 1, and 5 percent solutions of sulphuric acid. At intervals of time, the pH value of each solution was determined with the hydrogen electrode. For concentrations of acid greater than 1 percent, there

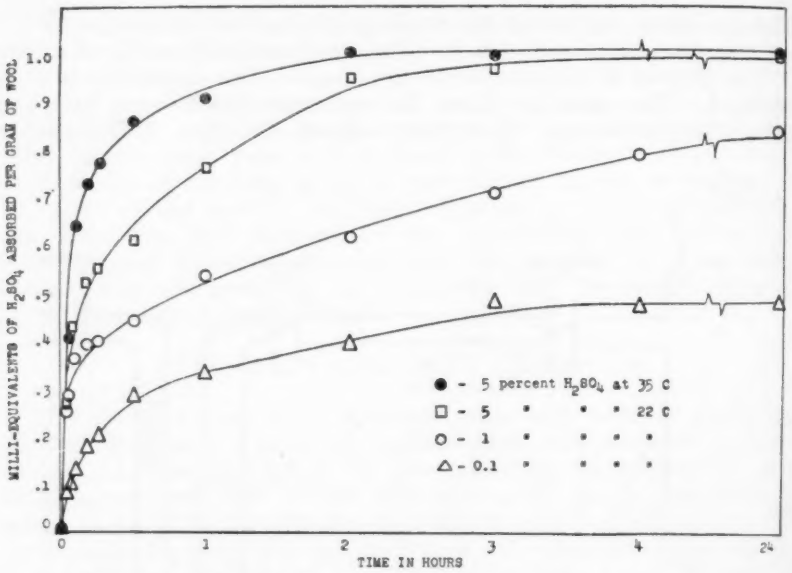

FIGURE 2.—*Rate of absorption of sulphuric acid by wool.*

was little if any variation in pH value because the quantity of acid taken up by the wool was very small compared with the amount present.

The amount of sulphuric acid absorbed by the wool as a function of time was determined. Specimens of the conditioned wool cloth containing 2 grams of wool protein were placed in flasks with 50 ml portions of sulphuric acid solution and the flasks were kept at a temperature of 22 C. The flasks were shaken frequently. At stated intervals, aliquots were taken from the flasks and titrated with standard sodium hydroxide solution. Only one aliquot was taken from each flask. The decrease in acid present in solution, or absorbed acid, obtained for each time interval is the average of three titrations. The results are shown in figure 2 in which the milliequivalents of absorbed acid are plotted as a function of time. The amount of acid

[5] Analyses of purified wool and of purified wool plus known amounts of sodium sulphate indicated that this method gives results satisfactory for present purposes. R. T. Mease, of the Bureau of Standards, is making a study of methods for analysis of wool for total and sulphate sulphur.

absorbed increases with increasing acid concentrations up to about 5 percent.

The curve through the solid circles in figure 2 shows the rate of absorption of acid by the wool cloth when soaked in a 5 percent solution of sulphuric acid at 35 C. The rate of absorption evidently increases with increase of temperature. However, the amount of acid absorbed at equilibrium is nearly the same as the amount absorbed in a 5 percent acid solution at 22 C.

2. WOOL-ACID-WATER SYSTEM WHEN THE WOOL IS DRIED

Specimens of wool were soaked in a 5 percent solution of sulphuric acid at 22 C for 3 hours and centrifuged for 3 minutes. They were then exposed to atmospheres of 9, 30, 65, and 90 percent relative humidities at 70 F. The samples were analyzed for sulphate, moisture and wool protein. The values in table 2 are given in grams per gram of wool protein at equilibrium and each is the average of three determinations.

TABLE 2.—*Moisture and sulphate contents of wool specimens treated with 5 percent sulphuric acid and exposed to atmospheres of different relative humidities at 70 F.*

[Quantities are per gram of wool protein]

Relative humidity	Moisture	Sulphate
Percent	*Gram*	*Gram*
9	0.0380	0.0813
30	.1118	.0810
65	.1372	.0806
90	.2484	.0810

The moisture contents of wool soaked in 2.5 and 5 percent solutions of sulphuric acid, centrifuged and dried to equilibrium with atmospheres of different relative humidities, and the moisture contents of similarly dried untreated wool are recorded in table 3.

TABLE 3.—*Moisture contents of acid-treated and untreated wool specimens after exposure to atmospheres of different relative humidities at 70 F.*

Relative humidity	H_2O per gram wool protein		Difference (3−2)
	Treated with 2.5% H_2SO_4	Untreated	
Percent	*Millimols*	*Millimols*	
6	1.98	2.47	0.49
30	5.19	6.19	1.00
65	7.37	7.98	.61
90	9.73	9.99	.26
	Treated with 5% H_2SO_4	Untreated	Difference
6	1.81	2.53	0.71
30	5.09	6.29	1.20
65	7.41	7.96	.55
90	10.04	10.22	.18

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The wool treated with sulphuric acid absorbs less moisture than untreated wool. The difference in the amount absorbed varies with the relative humidity, a maximum difference being reached between 6 and 65 percent relative humidity. This observation will be discussed later.

WOOL-ACID-WATER SYSTEM WHEN THE DRIED WOOL IS BAKED

Specimens of the wool cloth were soaked for 3 hours at 22 C in 2.5, 5.0, 7.5, and 10 percent solutions of sulphuric acid and centrifuged. They were exposed to atmospheres of different relative humidities and then baked for different lengths of time. Samples containing 40 percent or more moisture were obtained by squeezing the excess liquor from the wool. Samples prepared this way contained only a very slightly larger amount of acid. The moisture contents of duplicate specimens which were not baked were determined. The baking was done in a laboratory electric drying oven (inside dimensions 1 ft by 1 ft by 1 ft). A beaker of water was kept in the oven in order to maintain high relative humidity.

The breaking strengths and ammonia nitrogen contents of the specimens after baking were determined as already described. The results are given in table 4.

These data indicate that for each acid concentration there is a critical moisture content above which the breaking strength of the cloth decreases and the ammonia nitrogen content increases when the wool is baked. Thus the critical moisture content of wool soaked in 2.5 percent sulphuric acid is about 50 percent, for 5 percent acid about 40 percent, and for 7.5 percent about 30 percent. The increase in ammonia nitrogen serves as a more sensitive measure of the deterioration taking place during the baking process than decrease in breaking strength. This is evident from table 4 in which samples treated with 2.5, 5.0, and 7.5 percent sulphuric acid solutions and containing 3 percent moisture showed no decrease in tensile strength after baking, but showed appreciable increases in ammonia nitrogen content. Both the physical and chemical breakdowns increase with increasing acid concentration in the specimen and increasing temperature in the baking oven. The decrease in breaking strength resulting from baking is independent of the time of baking. This can be explained by the assumption that the moisture content drops below the critical value in the first few minutes of baking after which no further breakdown occurs.

TABLE 4.—*Effects of acid and moisture contents and time and temperature of baking on the breaking strength and ammonia nitrogen contents of wool specimens*

H_2O in specimen before baking	Time of baking	Temperature of baking	Breaking strength 1-in. strip	Ammonia nitrogen per gram of specimen after baking [1]
Percent	*Minutes*	*° F*	*Pounds*	*Milligrams*
Original			27	0.20
12	60	250	27	0.54
Wool soaked in 2.5% sulphuric acid (0.058 g H_2SO_4 per gram wool protein)				
3	60	250	27	.58
9	60	250	27	.54
12	60	250	27	.64
21	60	250	27	.59
30	60	250	27	.71
50	60	250	26	1.01
65	60	250	23	1.25
Wool soaked in 5% sulphuric acid (0.081 g H_2SO_4 per gram wool protein)				
3	60	250	27	1.06
9	60	250	26	.96
12	60	250	26	.98
21	60	250	27	.96
30	60	250	27	1.09
40	60	250	25	1.15
50	15	250	23	1.53
50	30	250	22	1.59
50	45	250	23	1.50
50	60	250	23	1.52
64	15	250	20	1.66
64	30	250	19	1.72
64	45	250	19	1.65
64	60	250	20	1.60
50	60	225	27	1.50
50	60	200	25	1.38
50	60	175	25	1.30
50	60	150	25	1.41
Wool soaked in 7.5% sulphuric acid (0.098 g H_2SO_4 per gram wool protein)				
3	60	250	27	1.38
9	60	250	26	1.49
12	60	250	27	1.33
21	60	250	24	1.47
30	15	250	14	2.33
30	30	250	16	2.30
30	45	250	15	2.51
30	60	250	14	2.42
50	60	250	9	3.19
Wool soaked in 10% sulphuric acid (0.117 g H_2SO_4 per gram wool protein)				
3	60	250	21	2.15
9	60	250	20	2.13
12	60	250	21	2.19
21	60	250	20	2.30
30	60	250	8	3.90
40	60	250	3	4.75
50	60	250	1–2	5.92

[1] Specimens conditioned at a relative humidity of 65% and a temperature of 70 F.

4. AGENTS WHICH INFLUENCE THE DETERIORATION OF WOOL IN BAKING

Specimens of the wool cloth were soaked in a 5 percent solution of sulphuric acid for 3 hours at 22 C, centrifuged, and air dried. The cloth was cut into strips (6 in. by 1 in.), and 4 strips were placed in each of 4 glass tubes (10 in. by 1.5 in.) which had been drawn out at the ends. The 4 tubes were treated as follows:

1. Evacuated with a high-vacuum pump for 4 hours and sealed.
2. Moist carbon dioxide (CO_2 bubbled through water) was passed through the tube for 2 hours. This tube was then sealed.
3. Same as (2) substituting oxygen for carbon dioxide.
4. Same as (2) substituting air for carbon dioxide.

The tubes were placed in an oven at 250 F for 1 hour.

Similar experiments were made using untreated wool. The results given in table 5 indicate that both oxygen and moisture promote the deterioration of wool during baking. Sulphuric acid increases the deterioration considerably.

TABLE 5.—*Effect of baking on untreated specimens of wool and wool treated with 5 percent H_2SO_4 for 3 hours at 22 C, in vacuo and in moisture saturated atmospheres*

Atmosphere in tube	Appearance of specimen		Breaking strength 1-inch strip		Ammonia nitrogen per gram of specimen	
	Treated	Untreated	Treated	Untreated	Treated	Untreated
			Pounds	*Pounds*	*Milligrams*	*Milligrams*
Vacuum	Slightly yellow	No change	21	27	6.4	0.20
Carbon dioxide	do	Very slightly yellow	15	26	10.5	1.29
Oxygen	Dark brown	Yellow	0	18	23.2	3.88
Air	Yellow	Very slightly yellow	6	23	12.5	2.32

5. EFFECT OF STORAGE ON THE DRIED WOOL

Specimens of the wool cloth were soaked in 2.5, 5.0, 7.5, and 10 percent solutions of sulphuric acid for 3 hours at 22 C, centrifuged, and stored in atmospheres of relative humidities of 6, 30, 65, and 90 percent. They were exposed to a low intensity, incandescent light. At intervals of time, the ammonia nitrogen contents and breaking strengths were determined. The physical and chemical breakdowns of the specimens on storage are shown in figures 3 and 4, respectively.

There is no evidence of any marked increasing physical breakdown of any of the acid-treated specimens on storage in atmospheres of 6 and 30 percent relative humidities. The data suggest the possibility of some break-down increasing with time of exposure with 90 percent relative humidity using 5, 7.5, and 10 percent solutions of sulphuric acid. The samples were weaker within 24 hours after treatment with acid than before treatment, this initial loss in strength being greater at the higher acid concentrations.

With the exception of the specimens treated with 2.5 and 5 percent solutions of sulphuric acid, and exposed to a relative humidity of 6 percent, all of the specimens showed increasing ammonia nitrogen contents during storage. The ammonia nitrogen content increased with increasing relative humidities, acid concentrations, and time of storage.

Here again it is shown that the ammonia nitrogen content gives a more sensitive measure of the deterioration taking place in the wool

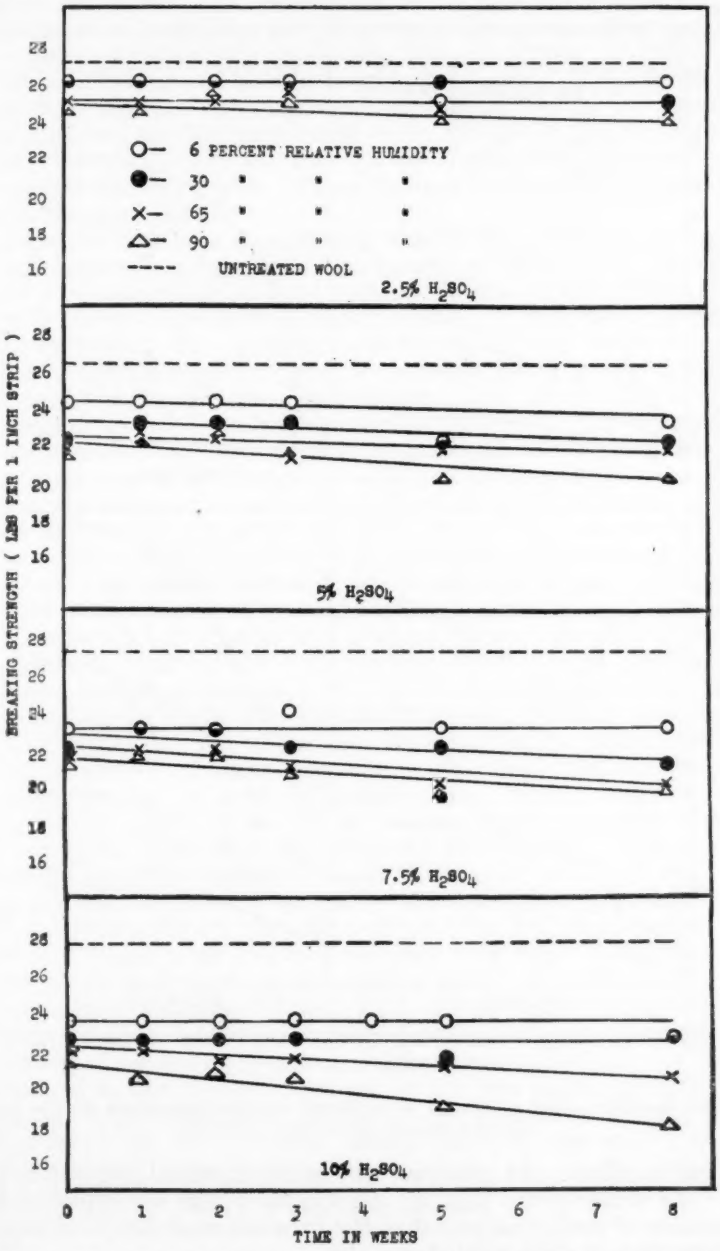
6 PERCENT RELATIVE HUMIDITY
30 " " "
65 " " "
90 " " "
UNTREATED WOOL
2.5% H_2SO_4
5% H_2SO_4
7.5% H_2SO_4
10% H_2SO_4
BREAKING STRENGTH (LBS PER 1 INCH STRIP)
TIME IN WEEKS
0 1 2 3 4 5 6 7 8
16 18 20 22 24 26 28

FIGURE 3.—*The effect of storage at different relative humidities on the breaking strength of acid-treated wool.*

cloth than the breaking strength. That ammonia is found during protein deterioration is well known. Lloyd [6] states that ammonia is

[6] D. J. Lloyd, Chemistry of the Proteins, p. 13, J. & A. Churchill, 1926.

always released during protein hydrolysis, apparently from the acid amide groups. Leiben and Urban [7] studied the splitting of ammonia from amino acids and other substances and found the ammonia cleavage proceeds much more rapidly in acid than in an alkaline or

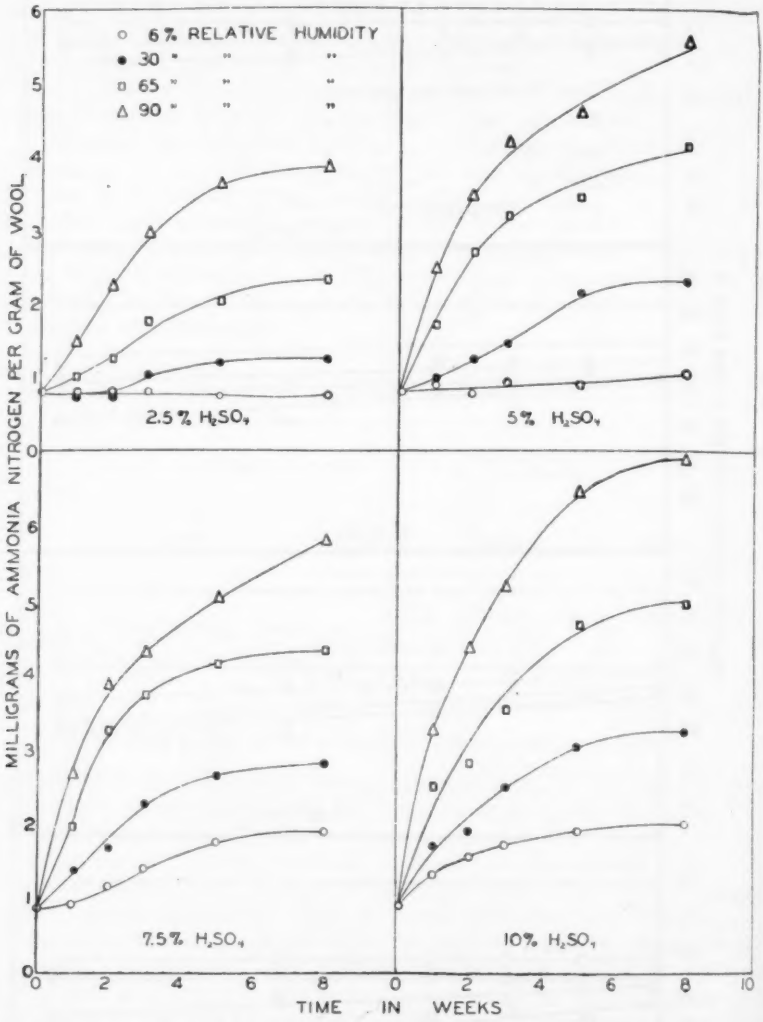

FIGURE 4.—*The effect of storage at different relative humidities on the ammonia nitrogen content of acid-treated wool.*

neutral medium. In studying the photochemical decomposition of silk [8] the writer found that the deterioration was accompanied by the formation of ammonia and that the greatest amounts were formed in a given time in acid-treated samples.

[7] F. Leiben and F. Urban, The Splitting of Ammonia From Amino Acids and Other Substances in the Light of a Quartz Lamp, Biochem. Zeit., vol. 239, pp. 250-6, 1931.
[8] Unpublished results.

IV. NATURE OF THE SYSTEM WOOL—SULPHURIC-ACID—WATER

The reaction of sulphuric acid with wool depends on the chemical constitution and molecular organization of the wool protein. Sulphuric acid may be taken up and held by wool in three ways. First, it may be chemically combined, the combined acid being bound by primary valence forces at the free amino and imino groups and at the peptide linkages. Second, it may be absorbed at micellar interfaces and held by secondary valence forces. Third, it may be absorbed in capillary spaces in the wool fiber.

Considerable evidence has been presented for both the chemical type and adsorption type of combination of acids with proteins.[9] Additional evidence that at least some of the acid is chemically combined with the wool protein was obtained in a study on the absorption of iodine by wool.[10] The iodine number of wool is 14.1. After the wool is soaked in normal sulphuric acid the iodine number is only 2.6. On rinsing the acid-treated wool in running water, the iodine number rises after 1 hour to 9.6 and remains at that value on continued rinsing. If an acid-treated specimen is first treated with a 1 percent sodium carbonate solution to neutralize the acid and is then rinsed, the iodine number is the same as that of untreated wool. Since the iodine reacts with the free amino groups of the wool, these observations indicate that the sulphuric acid combines with the free amino groups and occupies a place that would ordinarily be available to iodine. The combined acid is only removed by neutralization with alkali.

However, not all of the acid absorbed by the wool can be accounted for by assuming combination with the free amino groups. In figure 2 it is shown that wool treated with 5 percent sulphuric acid absorbs about 1 milliequivalent of acid per gram of wool. Meunier and Rey [11] employing a modification of the Van Slyke apparatus found wool to contain 0.57 percent of amino nitrogen. This would account for only 0.41 milliequivalent of acid. Speakman and Hirst [12] using similar technique concluded that the amount of free amino nitrogen obtained from wool approached a limiting value of 0.92 percent. This amount accounts for only 0.66 milliequivalent of the acid.

That the amount of acid bound by the free amino groups of proteins does not account for the total acid taken up has long been known. Hitchcock [13] found that gelatin combined with 0.89 milliequivalent of hydrochloric acid whereas deaminated gelatin combined with 0.44 milliequivalent. Osborne [14] found that the amount of hydrochloric acid taken up by edestin was roughly 5 times the amount calculated on the basis of the amino groups. Sturin [15] neutralizes about 8 times as much acid as can be accounted for by the free amino groups.

It is evident that a large proportion of the acid absorbed by wool is not accounted for by its free amino nitrogen content. Several

[9] W. Hoffman and R. Gortner, Physico-Chemical Studies on Proteins, Colloid Symposium Monograph, vol. 2, pp. 209–368, 1925. The Chemical Catalog Co.

[10] Unpublished work by H. A. Neville, W. Fritz, and Milton Harris.

[11] L. Meunier and G. Rey, Sur les Proprieté s de la Laine, Jour. Soc. Leather Trade Chem., vol. 11, pp. 508–519, 1927.

[12] J. B. Speakman and M. C. Hirst, The Constitution of the Keratin-Molecule. Trans. of the Faraday, Soc., vol. 29, pp. 148–164, 1933.

[13] Hitchcock, The Combination of Deaminized Gelatin with Hydrochloric Acid. Jour. Gen. Physiol. vol. 6, pp. 95–104, and 457, 1923.

[14] T. B. Osborne, The Basic Character of the Protein Molecule, Jour. Am. Chem. Soc., vol. 24, pp. 39–78, 1902.

[15] A. Kossel and F. Weiss, Zeit. Physiol. Chem., vol. 78, pp. 402–413, 1912. Uber das Sturin.

workers have shown that the residual combining capacity of proteins may be attributed to the peptide linkages [16] [17] and to the imino groups. It is probable that these groups also account for a portion of the acid in wool in excess of that necessary to react with the amino groups.

The absorption of moisture from the atmosphere by wool is, in general, very similar to the absorption of acids from solution. The amount of moisture absorbed depends upon the relative humidity; that is, the effective moisture concentration, whereas the amount of acid absorbed depends on the pH; that is, the effective hydrogen-ion concentration. Both also depend on the physical and chemical nature of the specimen under consideration. Analogously to the way

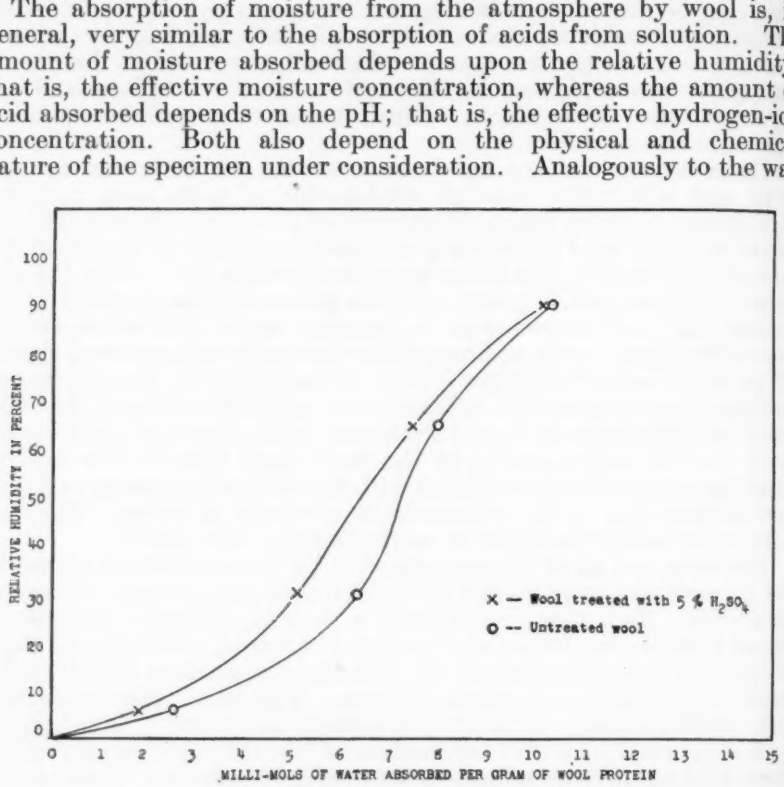

FIGURE 5.—*The absorption of water by untreated and acid-treated wool.*

in which wool takes up acids, it is assumed that moisture may be taken up in 3 ways; namely, by chemical combination, by adsorption, and by capillary condensation.

It is shown in table 3 that wool treated with sulphuric acid absorbs less moisture than untreated wool. Evidence is presented above that sulphuric acid combines with the amino groups of wool. It seems logical to conclude that the difference observed in column 4 of this table may be attributed either to combined sulphuric acid occupying places that would ordinarily be available to water, or that the combined and/or adsorbed acid has altered the forces capable of attracting the water.

Not all of the moisture taken up by the wool is combined or adsorbed, for if this were the case the two curves shown in figure 5 should lie parallel to each other. At the lower relative humidities the

[16] T. B. Osborne and C. S. Leavenworth, Protein Copper Compounds, Jour. Biol. Chem., vol. 28, p. 109, 1916.

[17] M. Siefried, Die Carbamino und Hydroxykohlensaurereaktion. Ergebnisse Physiol., vol. 9, p. 334, 1910.

moisture may be taken up largely by adsorption and chemical combination and these processes occur simultaneously. At higher relative humidities the third process also occurs, namely, the capillary condensation of moisture. At very high relative humidities, for example 90 percent, a large proportion of the moisture taken up is held by the capillary forces. Assuming that the acid in the wool has not changed the nature of these forces, both the acid-treated and untreated specimens would take up like quantities of moisture by this process. This would account for the converging of the two curves. The curves for wool treated with higher concentrations of sulphuric acid may cross at the higher relative humidities because of the hygroscopic nature of the excess of sulphuric acid present.

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COMPRESSION CUTTING TEST FOR RUBBER

By W. L. Holt

ABSTRACT

This paper describes a study of the compression cutting test, also referred to as the shear test, for rubber. The test consists of compressing a sample of rubber to failure between a flat plate or anvil and a cutting tool, and recording the relation between the thickness of the sample and the load up to failure. Data are presented on (1) different tools used for the test, (2) conditions affecting the results, and (3) a comparison of the compression cutting tests with other common tests. Advantages and disadvantages of the compression cutting test are discussed. The conclusion is reached that it is valuable as a supplement to, rather than as a substitute for, the tensile test.

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I. INTRODUCTION

Compression tests for insulated wire were described by Hippensteel in 1926.[1] Later Ingmanson and Gray [2] and Somerville [3] described a machine for making compression cutting and shear tests as applied not only to insulation for wire but to rubber in general. The test consists of compressing a sample between a flat plate or anvil and a cutting tool. The relation between the thickness under the cutting tool and the load is recorded graphically. The test has a strong appeal because it is much simpler to make than tensile-strength tests and data have been presented indicating that it may be a satisfactory substitute for the tensile test. The work described in the present paper was carried on in order to obtain information concerning the test with a view to employing it in specifications.

[1] Ind. Eng. Chem., vol. 18, pp. 409–411, 1926.
[2] India Rubber World, vol. 82, no. 4, pp. 53–56, July 1, 1930.
[3] Inst. Rubber Ind., Trans., vol. 6, no. 2, pp. 150–159, 1930.

II. DESCRIPTION OF MACHINE AND NATURE OF TEST

The machine used for the tests was the same as used by Ingmanson and Gray, and by Somerville. (See fig. 1.) It consists essentially of a means for compressing rubber samples between a cutting tool and a steel anvil and measuring the load and thickness under the tool. The tool is fixed at the top of the machine and the anvil carrying the sample is forced up against it as indicated. The load is applied through a heavy coil spring, the compression of which is used to measure the load. The lower end of this spring travels at a speed of 1.5 inches per minute. The compression of the spring (i.e., the load), together with the distance between the tool and the anvil (i.e., the thickness of the

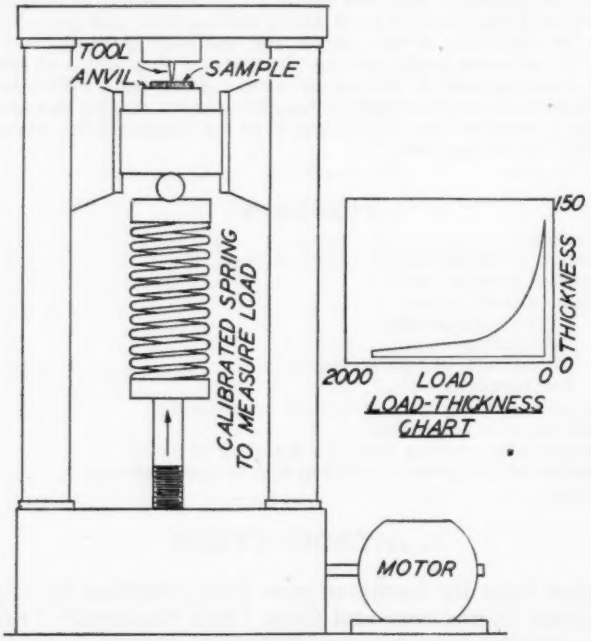

FIGURE 1.—*Machine for compression cutting tests.*

specimen), are recorded mechanically on a chart as a load-thickness curve. The maximum capacity of the machine is 2,000 pounds.

Cutting does not take place gradually as is the case with many materials. Instead, the rubber is compressed to a fraction of the original thickness before any cutting occurs. When cutting does start, it takes place suddenly and, due to the design of the machine, the specimen is cut completely through.

The property of a rubber compound measured by the test is not a simple one. The rubber is first crowded away from each side of the cutting tool, thus introducing stresses at an angle to the section being cut. The top surface of the sample is put in tension as indicated by the deformation of the surface, and frictional resistance between the rubber and the tool and anvil introduces stresses. The test is often referred to as shear, but in the present paper the expression "compression cutting", or simply cutting, is used as being a truer descrip-

tion. The test may be classed as a performance test in that it represents a condition which rubber may be called upon to resist in service. A relatively small quantity of material is required for test purposes, specimens are ordinarily easy to prepare, and small differences in the thickness of specimens have relatively little effect on the cutting load. Test specimens of insulation from wires and cables consist simply of longitudinal sections of the insulation about 1 inch long. Rubber in sheet form may be conveniently tested, a piece 1 by 2 inches sufficing for 6 or 8 tests.

III. COMPRESSION CUTTING TOOLS

A variety of ways of cutting have been tried out with the machine. When insulated wire containing a solid conductor is tested, it is satisfactory to compress the wire between two flat anvils. In this case, cutting takes place between the conductor and the anvils. However, this method cannot be used for a cable having a stranded conductor, nor is it applicable to the testing of sheet rubber. For tests of insulation from a stranded conductor, the insulation may be split longitudinally and the test made on a portion of the insulation between a flat anvil and a mandrel equivalent to the original wire size. For simplicity, however, there is an advantage in one tool for all tests, i.e., all sizes of wire, sheet rubber, etc.

A 90° steel wedge with the edge flattened to a width of 0.008 inch has been used elsewhere and was tried out for our work. (See fig. 2.) Questions arose, however, as to the necessary limits for the width of the flattened edge and how to define the sharpness of the two edges resulting from the flattening process. A series of wedges was made as nearly identical as possible except for the width of the flattened edges. These varied from 0.0008 to 0.0098 inch. Cutting tests were then made on five different compounds. The results are shown in figure 2. Duplicate tests were made with the samples dry and when lubricated with a mixture of glycerine and graphite. In both cases the relation between the width of the cutting edge and the cutting load is very nearly linear. A change in width of the cutting edge does not affect all compounds the same. The average for the dry tests with wedges in the region of 0.008-inch width is about 100 pounds difference in cutting load per 0.001-inch difference in width. With the lubricated samples it is about 85 pounds instead of 100 pounds.

An examination of wedges with a microscope after 40 or 50 tests showed considerable scratching of the surfaces, and a decided dulling, apparently due to high concentration of load on the edges of the flattened portion during a test. Attempts which were made to construct duplicate wedges indicated that considerable difficulty would be experienced in making them with equal cutting characteristics.

On the basis of these tests the 90° wedge was abandoned and a tool was made with an edge which can be more easily defined and renewed. This tool consists of an acute-angle wedge grooved along its edge to hold a piece of 1-millimeter drill rod. The tool and the corresponding anvil are shown in figure 3. Experience has shown that the tool can be easily duplicated and that by renewing the drill rod when there is an appreciable wear, a constant cutting edge is maintained. From the standpoint of cutting, the tool is equivalent to the mandrels used by Ingmanson and Gray. No precise data

have been obtained on the life of the cutting edge, but with ordinary grades of rubber, 100 tests per edge seem to be feasible. Stops are provided on each side of the cutting tool. These are set for a clearance of 0.002 inch between the tool and the anvil so as to avoid damage to the edge.

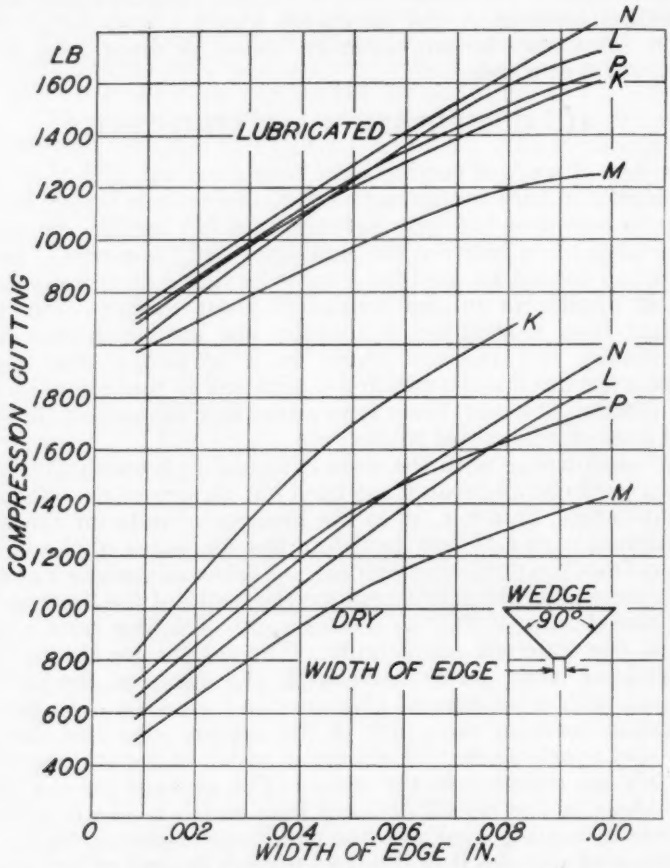

FIGURE 2.—*Relation of width of edge face to the compression cutting load.*

Five different compounds were tested as follows:
K—Pure gum, ultra accelerator.
L—Tread stock, 30 parts carbon.
M—Superaging compound 80 percent rubber by volume.
N—Tread stock, 50 parts carbon.
P—Loaded stock, 100 parts soft carbon.
In upper set samples were lubricated with glycerine and graphite. In lower set they were tested dry.

IV. CONDITIONS AFFECTING TEST

1. ADJUSTMENT OF TOOL

Care must be taken to insure that the tool and anvil face are parallel as otherwise low cutting loads result. The necessary limits for parallelism will depend upon the type of rubber tested and on its thickness. Tests show that for ordinary purposes the tool and the anvil should not be out of parallel by more than 0.001 inch. The thinner the sample and the more compressible the rubber, the greater will be the influence of any departure from parallelism.

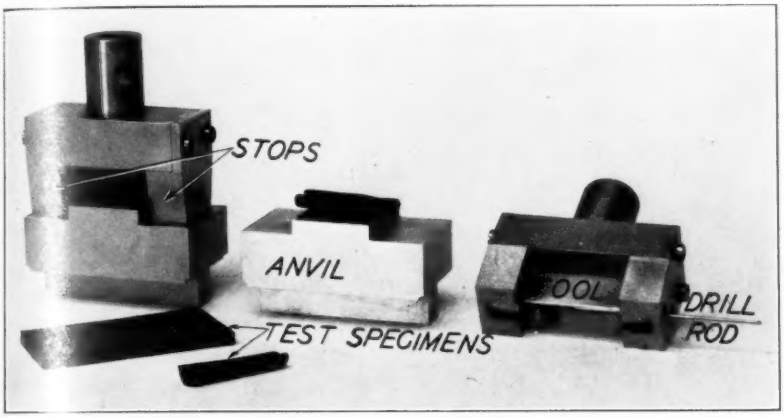

FIGURE 3.—*Tool and anvil used in compression cutting tests.*

Stops are set for .002" clearance between tool and anvil so as to avoid damage to edge.

2. LUBRICATION

As has been observed by previous investigators, if the surfaces of the specimen are lubricated, or if the compound tested contains a lubricant which blooms or exudes on the surface, the cutting load is lower than would otherwise be the case. Tests which were made on two compounds to show the influence of surface lubricants are shown in figure 4. When alcohol and water were employed, a container was constructed around the anvil, and tests were made with the sample completely submerged. In the other cases the tool and the anvil and both sides of the sample were coated with the lubricant.

The pure gum compound is more sensitive to surface lubrication than the tread stock. It also appears that the surface of the pure gum rubber may have been attacked by the vaseline during the 3 or 4 minutes necessary to make the tests, thus lowering the cutting load. The tread stock, being more resistant to a lubricant such as vaseline, showed the same cutting load with vaseline as with castor oil which does not affect rubber. The high sensitivity of pure gum to surface lubrication is also illustrated by the wedge tests in figure 2 where "K" acts very differently in the dry and in the lubricated conditions.

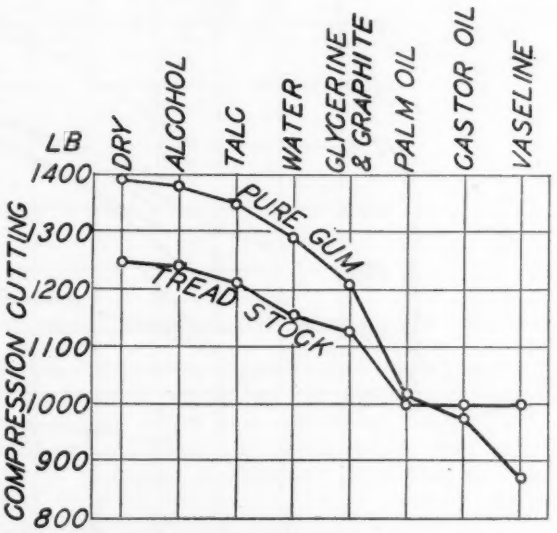

FIGURE 4.—*Influence of surface lubricants on the compression cutting load.*

Sheet rubber samples of pure gum rubber 0.087 inch thick and tread rubber 0.075 inch thick were tested with the substances indicated as surface lubricants. Each point shown is the average of 5 or more tests.

It is general practice in some laboratories to test all samples under water—a method well adapted to tests at different temperatures. In the present work all tests were made dry, the only precaution being to dust samples lightly with talc. This dusting appears to leave the surfaces of all samples in a similar condition. With many compounds, particularly if there is a slight bloom, the talc has little or no effect. With nonblooming stocks having very clean surfaces, the use of talc reduces the cutting load somewhat and seems to increase the consistency of a series of tests.

3. DIMENSIONS OF TEST SPECIMEN

The dimension of the test specimen in the direction of the cut should be slightly greater than 1 inch (the anvil is exactly 1 inch wide). The other dimensions may be dependent upon the material to be tested and of any convenient magnitude. With the renewable edge tool this design proved to be more practical than the older design in which the

cutting face was made an exact length, the method used with the wedge and other tools.

The thickness of the sample will affect the cutting load, but, as indicated previously, not in direct proportion to the thickness. Data on the effect of thickness are shown in figure 5. Tests were made on eight rubber compounds, subsequently described, each compound being cured in sheets of four thicknesses. Results reported by Somerville, and by Ingmanson and Gray are indicated in the figure by broken lines. There is some variation in the effect of thickness of different types of rubber on the cutting load, but as an average the load increases 25 to 35 percent for an increase of 100 percent in thickness.

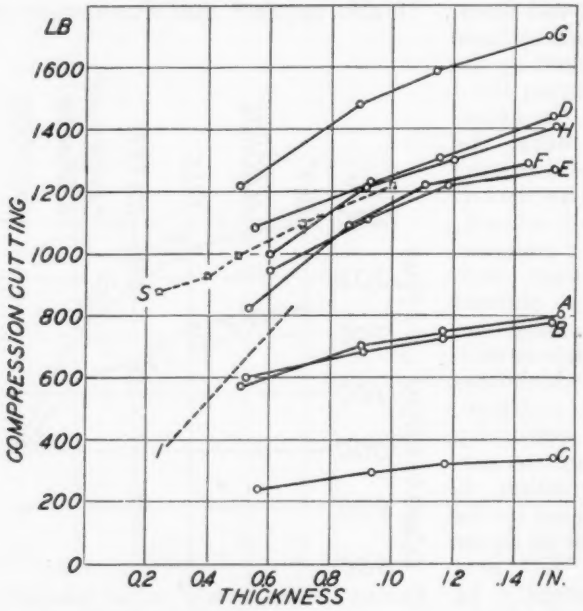

FIGURE 5.—*Influence of thickness of sample on the compression cutting load.*

Eight different compounds were tested (see table 1) with the tool shown in figure 3. Each point on the curve is the average of from 4 to 8 tests.

A. 30-percent insulation.
B. 40-percent insulation.
C. Low quality insulation.
D. 40 parts gas black stock.
E. 40 parts thermatomic carbon stock.
F. Pure gum plus 10 volumes kalite.
G. Pure gum, ultra accelerator.
H. Pure gum.
Broken line "S" shows results reported by Somerville with a wedge tool.
Dot-dash line "I" shows results reported by Ingmanson and Gray with a mandrel.

4. TEMPERATURE

Somerville has reported some data on the effect of temperature, which indicates that the compression cutting load and the tensile strength are affected similarly. In the present work all tests were made at a constant temperature of 75 F, and no data are presented on the effect of temperature.

V. COMPRESSION CUTTING TESTS OF TYPICAL COMPOUNDS

For a study of the compression cutting test as a means of classifying different types of rubber the eight compounds shown in table 1 were prepared in the form of sheets, several cures of each compound being made. The results of tests on these compounds are shown in figure 6.

TABLE 1.—*Composition of compounds tested*

Ingredient	Composition (parts by weight) of compounds—							
	A [1]	B [2]	C [3]	D	E	F	G	H
Rubber	100	100	250	100	100	100	100	100
Sulphur	4.6	4.0	11.72	3	3	2	2	3
Zinc oxide	37.0	32.6	15.60	5	5	2	2	2
Whiting	176.0	104.4	594.0					
Kalite no. 3 [4]						26.0		
Tetramethylthiuramdisulphide						.25	.25	
"Micronex" (carbon black)				40				
"Thermatomic" (carbon black)					40			
Stearic acid			3.91	4	4			
V.G.B. (antioxidant)	.5	.5		1	1			
Mercaptobenzothiazole			3.13	.8	.8			
Mineral rubber			235.0	5	5			
Tetramethylthiurammonosulphide	.4	.3						
Paraffin		5.5						
Ozokerite	4.1							
Litharge	8.2							
Reclaimed rubber			250.0					
Clay			235.0					
Diphenylguanidine								.75

[1] 30 percent insulation. [2] 40 percent insulation. [3] Code wire. [4] Specially processed calcium carbonate.

The accelerated pure-gum compounds G and H give the highest cutting loads. Ten or fifteen percent below the pure-gum compounds are D, E, and F, all containing fillers and consisting, respectively, of 40 parts of reinforcing carbon black, 40 parts of nonreinforcing carbon black, and 26 parts of kalite, a specially processed calcium carbonate. D, the tread type of compound, has a slightly higher cutting load than the other two compounds.

B and A are respectively 40 and 30 percent rubber insulation compounds. The cutting load of B is lowered by its paraffin content. Compound C is low in rubber and high in asphaltic materials and other ingredients and shows a low cutting load. Cure affects the cutting load in much the same way that it affects tensile strength.

The cutting load itself is not particularly sensitive in distinguishing among different types of compounds as evidenced by the relatively small differences among the five highest compounds that differ very materially in composition. It would appear that in order to distinguish among them some other factor should be taken into consideration, such as the thickness under the tool at the time of cutting or the rate of decrease in thickness with load. This conclusion is in line with tensile tests where elongation and stiffness, together with tensile strength, are used in attempting to define a compound.

Although the design of this machine is such that the thickness under the tool during compression is indicated graphically, the precision of the measurement for highly compressible rubber, particularly if thin, is not very great. However, several measurements of thickness under the tool at the instant of cutting were determined as

closely as possible. These showed that a pure-gum compound will decrease to about 8 percent of its original thickness, and a carbon black compound to about 12 percent of its original thickness before cutting takes place. If the surfaces are lubricated, these percentages will be about 6 and 10 percent, respectively. Other types of compounds, containing other ingredients, showed thicknesses at the time of cutting in about the same range. It appears that the thickness at the time of cutting is largely a function of the amount of mineral filler and that for any particular compound it is a constant percentage of the original thickness.

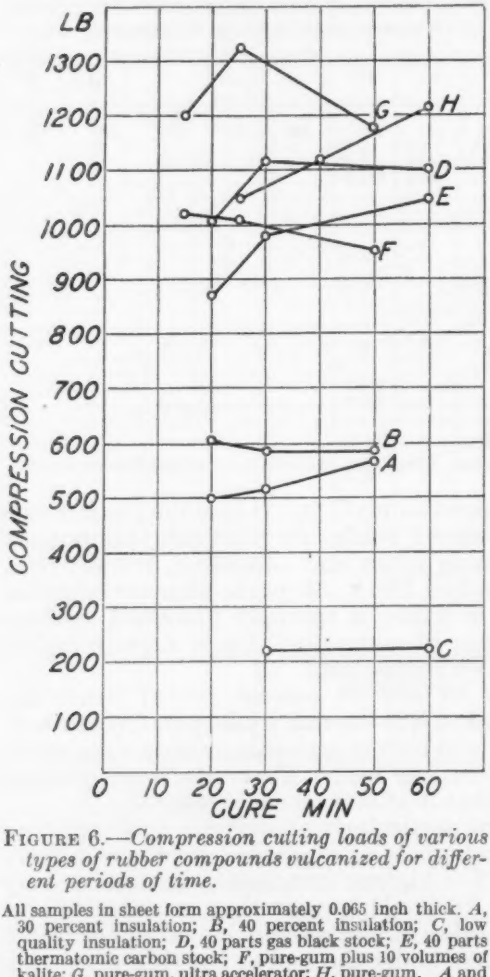

FIGURE 6.—*Compression cutting loads of various types of rubber compounds vulcanized for different periods of time.*

All samples in sheet form approximately 0.065 inch thick. *A*, 30 percent insulation; *B*, 40 percent insulation; *C*, low quality insulation; *D*, 40 parts gas black stock; *E*, 40 parts thermatomic carbon stock; *F*, pure-gum plus 10 volumes of kalite; *G*, pure-gum, ultra accelerator; *H*, pure-gum. *A* and *B* were vulcanized at 270 F; *F* and *G* were vulcanized at 275 F; *C*, *D*, *E*, and *H* were vulcanized at 288 F.

The method of measuring the thickness under the tool afforded by the machine, however, is not sufficiently precise on account of the magnitude of possible errors in the recording mechanism and elastic deformations in the machine, in comparison with the high degree of precision required. For instance, a sample of pure-gum rubber, 0.040-inch thick, will have a thickness under the tool of about 0.003 inch at the time of cutting. To make this latter measurement within 10 percent would necessitate a precision of measurement of 0.0003 inch, whereas the elastic deformation in the machine may be of the order of 0.0015 inch. However, for relatively thick samples and those containing a considerable volume of loading material the thickness at the time of cutting, as indicated by the machine, is sufficiently accurate for practical purposes.

Some check measurements of thickness under the tool were made by mounting a dial gage on the top of the machine with the foot extending through the top and resting on the anvil. The measurements, however, required a correction to take care of elastic deformation. A better plan would appear to be to redesign the head of the machine so as to permit precise gages accurate to 0.0001 inch to be mounted on each side of the tool and the anvil and very close to them.

VI. COMPARISON WITH OTHER TESTS

With the compounds shown in table 1, a comparison was made between compression cutting tests (both dry and with a lubricant), and corresponding tensile, tensile-product, and tear tests. The results are shown in figure 7. The cutting load, either in the presence or absence of a lubricant, is not directly related to any of the other tests. There are certain agreements with tensile and tensile product, and at the same time certain discrepancies. For instance, samples G and D, pure-gum and tread compounds, respectively, are reversed in the cutting and the tensile tests; sample F is high in tensile product, and sample C is low as compared with the cutting tests.

The tear test is entirely out of line with the cutting test.

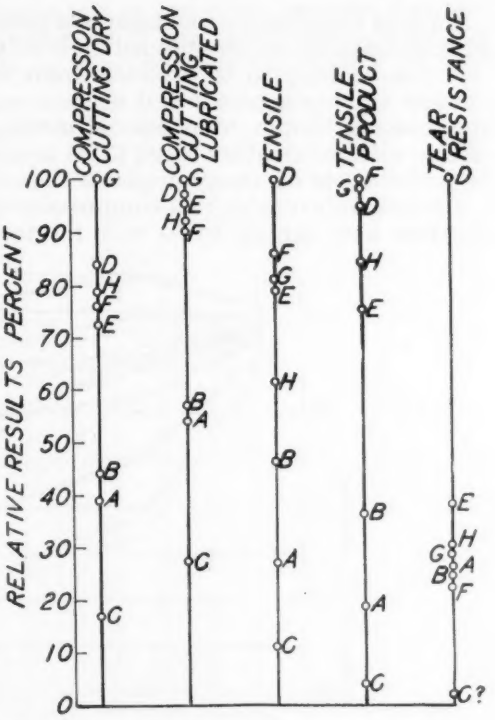

FIGURE 7.—*Comparison of tests by different methods.*

Letters indicate compounds listed in table 1. Tests were made on the intermediate cures of all compounds except *C* and *H*. The shortest cures of these were tested. (See figure 6.) Tensile product is equal to the tensile strength multiplied by the elongation at break: *A*, 30 percent insulation; *B*, 40 percent insulation; *C*, low quality insulation; *D*, 40 parts gas black stock; *E*, 40 parts thermatomic carbon stock; *F*, pure-gum, plus 10 volumes kalite; *G*, pure-gum, ultra accelerator; *H*, pure-gum.

VII. THE COMPRESSION CUTTING TEST AS A MEASURE OF AGING

The change in tensile strength over a period of exposure to accelerated aging conditions is the usual measure of the aging properties of a rubber compound. Tests were made to ascertain the possibility of substituting the compression cutting test for the tensile test in measuring aging properties. The same 8 compounds shown in table 1 were used and the cutting loads and the corresponding tensile strengths were determined after 0, 7, and 21 days in an oven at 70 C. The results are shown in figure 8.

As indicated by the figure, the changes in the cutting load follow in a general way the changes in tensile strength, but in practically every case they are less than for tensile strength. Taking an average for all 8 compounds, there is a drop in tensile strength of 38 percent and a drop in the cutting load of 25 percent over the 21-day period. This means that the cutting test is about 65 percent as responsive to differences as the tensile test.

Stress-strain tests which were made on these compounds during aging show that A, C, D, and E stiffen and B, F, G, and H soften. Those which stiffen retain relatively high cutting loads, and those which soften show a considerable reduction in the cutting load.

VIII. APPLICATION OF COMPRESSION CUTTING TEST TO SPECIFICATIONS

Factors favoring the inclusion of a compression cutting requirement in specifications can be summed up briefly as follows: (1) The cutting test can be adapted to products from which it is difficult or inconvenient to obtain tensile test specimens; (2) the preparation of test specimens is simple—dimensional measurements need not be as precise as with many other tests; (3) it is more nearly an actual measure of performance for many products than tensile strength tests.

Factors unfavorable to a compression cutting requirement in specifications have largely to do with the technical details of making the

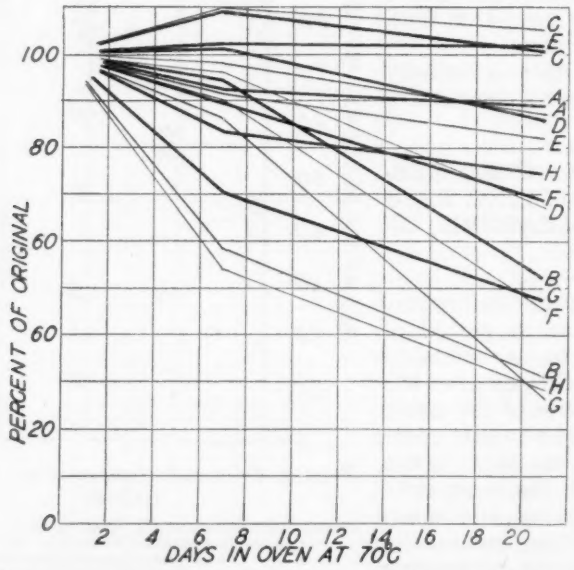

FIGURE 8.—*Influence of aging in an oven on compression cutting and tensile strength.*

Letters refer to compounds in table 1: *A*, 30 percent insulation; *B*, 40 percent insulation; *C*, low quality insulation; *D*, 40 parts carbon black stock; *E*, 40 parts thermatomic carbon stock; *F*, pure-gum plus 10 volumes kalite; *G*, pure-gum, ultra accelerator; *H*, pure-gum. Heavy lines show results of compression cutting tests. Light lines show results of tensile tests.

test. They may be stated briefly as follows: (1) Its use with thin samples, 0.006 to 0.020 inch in thickness, is open to question. The thickness of such samples at the time of cutting would be as little as 0.0005 to 0.0016 inch. For parallel cutting this requires tools and alinement of a degree of perfection that is perhaps beyond the range of practicability. In addition, the stops which protect the edge of the tool would probably have to be removed or adjusted within extremely close limits; (2) careful consideration must be given to the presence or absence of lubricants on the surface of the rubber. The use of a lubricant tends to make the cutting loads for different

types of compounds more nearly the same and reduces the sensitivity of the test; (3) as a criterion of aging in an oven, the cutting test is less responsive to differences than the tensile strength test.

IX. CONCLUSION

Compression cutting may be used to advantage in testing certain types of rubber products and in studying specific problems, but it is not the equivalent of the tensile test or any other common test used for rubber. From the data obtained in this study compression cutting appears to be valuable as a supplement to present tests for rubber goods.

WASHINGTON, January 8, 1934.

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WEAR OF DIES FOR EXTRUDING PLASTIC CLAY

By R. T. Stull

ABSTRACT

Dies of 21 materials were investigated and the following determinations made: approximate taper or "angle of wear" of the dies necessary to produce constant wear losses, relation between wear loss and extrusion pressure, relative service values, Vicker's hardness numbers, the decrease in wear resistances of nitrided steel and porcelain due to their hard outer portions, and the relative abrasive intensity of a plastic porcelain body as compared to that of a plastic clay-sand mixture.

The angle of constant wear rate was found to be approximately 3.58°. The relative service values ranged from 3.22 for a soft brass to 1,673 for an alloy composed of cobalt, chromium, and tungsten. The wear resistance of porcelain decreased asymptotically with depth, and the wear resistance of nitrided steel varied irregularly as successive layers of the case were removed by abrasion. There was no correlation between service values and Vicker's numbers for unlike materials, but there was, in general, a direct relation between the two properties for materials of the same kind. The relative wear loss of any one material is equal to the 1.548th power of the extrusion pressure divided by a constant.

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I. INTRODUCTION

In the "stiff mud" process for manufacturing clay products, the clay in the stiff plastic condition is extruded through a die from which the clay issues in the form of a continuous bar or column which is then cut by wires into proper lengths for brick, tile, porcelain tubes, or whatever product is being made.

Most clays are highly abrasive in character, causing rapid wear of the dies so that frequent renewals are necessary in order to maintain uniformity in size of product. The predominating abrasive material in clays consists of quartz grains or silica sand, of which from less than 1 percent to more than 50 percent may be present.

No data were available regarding the wear resistance of dies to plastic clay and it was for the purpose of obtaining such data that this investigation was undertaken.

The laboratory tests were made in a manner to simulate practical working conditions. The materials were made in the form of dies and a definite volume of clay was forced through the dies during each test at a constant volume rate. With a new die the length of clay column produced per unit of time was equal to the length of column from an auger machine producing approximately 7,000 side-cut face brick per hour.

II. MATERIALS INVESTIGATED

1. TYPE AND HISTORY

The most commonly used materials for dies in the clay industry are cast iron and high carbon steel, both comparatively inexpensive. Specimens of these materials and also others not so commonly used were included in the investigation. The materials included were 1 brass, 1 copper, 4 cast irons, 3 stainless steels, 5 differently heat-treated specimens of a chromium tool steel, 1 high carbon steel, 1 chromium-molybdenum steel, 3 chromium-cobalt-tungsten alloys, 1 nitrided steel, and a porcelain.[1] The chemical composition and history of each specimen are given in table 1.

[1] Chromium-plated cold rolled steel dies were also included. The plating wore through in spots, "chipping" followed, and no satisfactory value was obtained.

TABLE 1.—*Chemical composition, source, and heat treatment of dies investigated*

Specimen no.	Graphitic C	Total C	Cr	Mo	Co	Mn	Ni	W	Al	Si	P	S	Remarks
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	
3	------	1.50	12.50	1.10	0.60	0.50	0.20	------	------	0.30	------	------	Chromium-molybdenum steel. Dies made by the manufacturer. Mill analysis.
4	------	.30	1.09	.24	------	.54	.12	------	0.91	.56	0.02	0.02	Nitrided steel. Dies made by the manufacturer, and nitrided for 48 hours at 975 F by Dr. Victor O. Homerberg, division of physical metallurgy, Massachusetts Institute of Technology. Analysis by chemistry division, Bureau of Standards.
5	3.26	3.95	------	------	------	.71	------	------	------	2.85	.79	.03	Cast irons. Dies machined from castings made by the metallurgical division and analyses by the chemistry division, Bureau of Standards.
6	3.12	3.72	------	------	------	.57	------	------	------	2.24	.46	.08	
7	2.95	3.57	------	------	------	.24	------	------	------	2.80	.83	.02	
8	2.86	3.73	------	------	------	.18	------	------	------	1.63	.49	.02	
11	------	------	35	------	50	------	------	10	------	------	------	------	Cobalt-chromium-tungsten alloys. Dies and "type composition" supplied by the manufacturer. Nos. 12 and 13 were cast by different methods which were not revealed.
12	------	------	30	------	50	------	------	15	------	------	------	------	
13	------	------	30	------	50	------	------	15	------	------	------	------	
14	------	.12	12.22	------	------	------	.24	------	------	------	------	------	Stainless steels. Dies made by the manufacturer. No. 15, annealed. No. 16 hardened by rolling. Mill analyses.
15	------	.09	18.46	------	------	------	8.83	------	------	------	------	------	
16	------	.09	18.46	------	------	------	8.83	------	------	------	------	------	
17	------	1.00	------	------	------	2.90	------	------	------	.13	.02	.02	High-carbon steel. Dies made from stock (S.A.E. 1095). Mill analysis. Dies heated to 1450 F, quenched in water and tempered to 500 F. Heat treatment by metallurgical division, Bureau of Standards.
19	------	.97	3.90	------	------	.20	------	------	------	.37	.02	.02	Chromium tool steel. Dies made and heat treated by a manufacturer of porcelain. Mill analysis. Heat treatment: no. 19, annealed; no. 20, heated to 1050 F and hardened in air blast; no. 21, heated to 1650 F and hardened in air blast; no. 22, heated to 1750 F, hardened in air blast and drawn to 750 F; no. 23, heated to 1750 F, hardened in air blast and drawn to 1150 F.
20	------	.97	3.90	------	------	.20	------	------	------	.37	.02	.02	
21	------	.97	3.90	------	------	.20	------	------	------	.37	.02	.02	
22	------	.97	3.90	------	------	.20	------	------	------	.37	.02	.02	
23	------	.97	3.90	------	------	.20	------	------	------	.37	.02	.02	

	Cu	Zn	Ni	Mn	Fe	Sn	Al	Pb	
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	
9	99.80	------	------	------	------	------	------	------	Copper. Dies machined from electrolytic copper cast by the metallurgical division, Bureau of Standards. Approximate analysis.
10	49.70	45.14	1.95	1.33	0.97	0.60	0.22	0.11	Brass. Dies machined from a piece of ship propeller blade of German origin. Analysis by chemistry division, Bureau of Standards.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	
24	49.60	45.20	1.85	1.20	0.54	0.16	0.80	0.08	0.55	Porcelain. Dies and approximate analysis supplied by the manufacturer.

(a) NITRIDED STEEL

Photomicrographs of nitrided steels [2] have shown that their cases are composed of distinct layer-like parts corresponding to different degrees of hardness according to the hardness numbers. This indicated that variable wear would be encountered with depth of material removed as wear progressed, and the nitrided steel was, therefore, included for a study of its wearing behavior.

(b) PORCELAIN

In a certain factory the dies for extruding spark plug blanks were made of chromium tool steel. In searching for a more serviceable die material a die was made of the spark plug body and heated in the kiln with the regular product. The die was given a service test in comparison with the steel die. The latter, producing 30,000 blanks a day for 35 days, had extruded approximately 66 miles (103.8 km) of material and had enlarged 0.016 inch (0.406 mm). The porcelain die, used for 85 days, had extruded approximately 160 miles (275.5 km) of material and had enlarged 0.020 inch (0.508 mm). Two unglazed dies of the same porcelain as the experimental plant die were submitted by the manufacturer for tests.

The porcelain dies were formed by molding, in the plastic condition, drying and machining to size, making proper allowance for shrinkage during heating. The machining removed the original surface of the dry porcelain body and, therefore, the factors set forth by Navias [3] as being responsible for the so-called "skin" were eliminated. The porcelain was included for the purpose of determining its wearing behavior and also whether a skin not ascribable to the finishing process was developed during the heating process and, if so, whether its presence would be indicated by changes in wear resistance with depth.

III. EQUIPMENT AND TEST METHODS

1. DIES

(a) FACTORS INFLUENCING WEAR

For a definite volume of clay extruded under constant working conditions, the wear depends upon the amount of abrading area of the clay contacting and sliding over the working face of the die and the pressure under which that area is acting. The greater the magnitude of either of these two factors, the greater is the wear. Inasmuch as the pressure which is greatest at the die entrance drops as the clay passes through the die, the wear is greatest near the orifice [4] entrance and diminishes toward the exit.

For a definite volume of clay extruded the area of the clay passing any transverse cross section of a cylindrical orifice is obviously the same. As the orifice entrance enlarges in wearing from the cylindrical

[2] Trans. Am. Soc. Steel Treating, vol. 16, no. 5, 1929, Nitriding Edition.

[3] "During the molding, finishing and drying processes, the very fine particles of materials are brought to and rubbed over the surface, and in the firing process they form a vitreous skin, often more vitreous than the interior of the specimen"; Metal porosmieter for determining the pore volume of highly vitrified ware, Jour. Am. Cer. Soc., vol. 8, no. 12, p. 818, 1925.

[4] In this report the term "orifice" designates the opening through the die.

toward the tapered form, the abrading area of a definite volume of the clay increases as it passes through the orifice, thus tending to increase wear, but at the same time it is acting under diminishing pressure. When a certain balance occurs between the actions of increasing wear due to increasing clay area and decreasing wear due to decreasing pressure as the clay passes through the die, then that taper or "angle of constant wear rate"[5] has been developed where a layer of substantially uniform depth is removed.

(b) DEVELOPMENT OF TAPERED ORIFICE AND RELATION BETWEEN WEAR RATE AND TIME EQUIVALENT IN WEARING FROM CYLINDRICAL TO TAPERED FORM

In the preliminary work the dies were made with cylindrical orifices ¼ inch (6.35 mm) in diameter and 1-inch long (25.4 mm). The wear loss was small at first, increasing with successive tests and apparently approaching a constant value. During the first test the wear was confined close to the die entrance and, in successive tests, gradually approached the exit. With a cast-iron die (no. 2) of unknown composition, the exit end of the orifice showed no increase in diameter until the fifth test, when a very small increase was observed.

Figure 1, representing a longitudinal cross section of the die and protecting ring,[6] illustrates the manner in which the wear progressed. The curves represent approximately the outlines of consecutive portions removed, the decreasing curvature suggesting that wear was progressing toward some definite form of tapered orifice. The wear losses of the last four tests were approximately in agreement and the angle of taper, determined by micrometer measurements of plaster casts, was found to be 3.55°.[7]

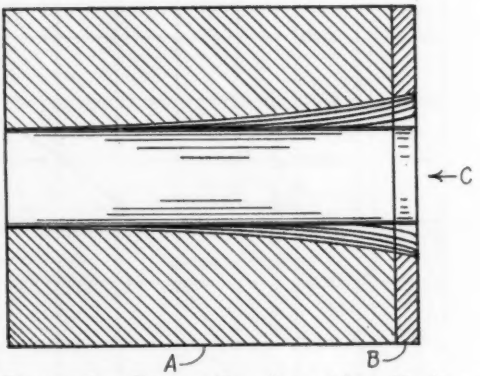

FIGURE 1.—*Cross section of a cast-iron die showing approximately the progression in wearing from an orifice of cylindrical form toward a tapered orifice of constant wear rate.*

A, die; B, protecting ring; C, entrance.

In figure 2 the relative wear rate[8] is plotted against the number of the test, which is equivalent to plotting against units of time inasmuch as each test required substantially the same time (32 ± ⅛ minutes). The relation between relative wear rate and time equivalent in wear-

[5] The angle of constant wear rate may be affected by the presence of local soft and hard spots in the die material. Where one solid is rubbing against another, the hard spots tend to shield the soft ones from wear. But plastic clay when flowing under pressure exhibits more of the properties of a liquid than it does of a solid and in moving over the die surface the clay wears the soft spots more rapidly than the hard ones; thus surface irregularities may be developed. Also, it has been observed in dies under factory conditions that when a scratch or groove occurs in the die, instead of smoothing out under continued wear it generally grows wider and deeper.

[6] Each die was provided with a protecting ring of the same material which was placed at the entrance end of the die to protect it from wear so that the measured wear would be confined to the die orifice. The protecting ring was located in the same relative position as the "die plate" or "bolting plate" of factory-operated dies.

[7] The measurements were made to the nearest 0.0005 inch; hence the results are accurate to approximately ±0.03°.

[8] Relative wear rate is defined on p. 511.

ing from cylindrical form to the taper of constant wear rate is of the form:

$$(a+u)\ (b-v)=R$$

in which u is time equivalent, v is relative wear rate, and a, b, and R are constants. The values obtained for these constants which conform closely to the data are:

$$a=2.473,\ b=0.04568,\ R=0.113$$

Theoretically, the value of the asymptote $v=b=0.04568$, represents the constant wear rate of the die. Evidently the die when measured

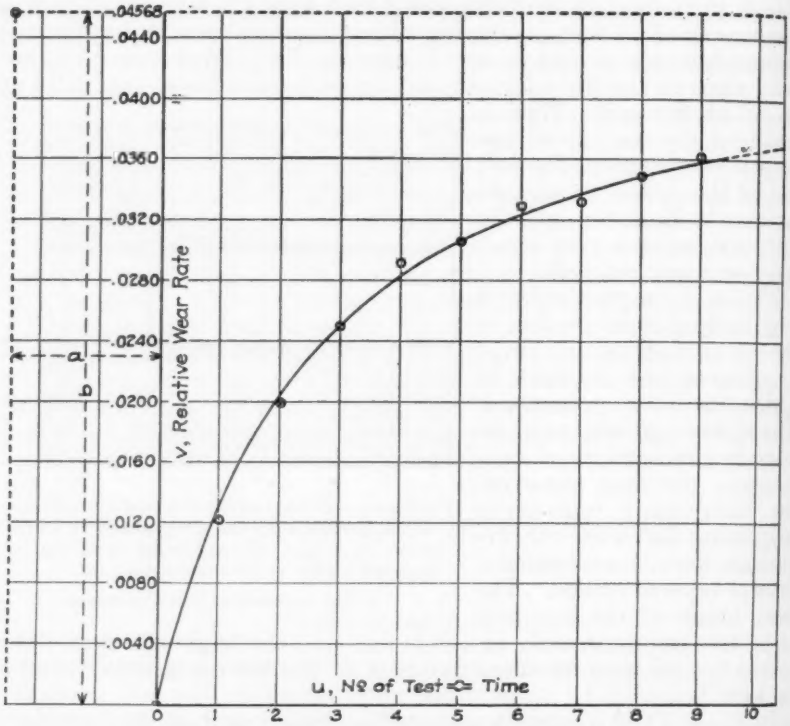

FIGURE 2.—*Relation between relative wear rate v and time equivalent u for cast-iron die no. 2 in wearing from the cylindrical orifice toward the tapered orifice of constant wear rate.*

after the ninth test had not attained the angle of constant wear rate. Theoretically, this would require that the die be operated under constant conditions for an infinite time.

(c) ANGLE OF ORIFICE ADOPTED FOR TEST DIES

It was desirable that the orifice of the die specimens be made to such a taper as would give wear losses comparable within the inherent errors of measurement. Therefore, 8 dies consisting of 2 each of the brass, cast irons nos. 5 and 6 and stainless steel no. 14 were made with tapered orifices of 3.58° [9] and when subjected to the wear tests pro-

[9] This taper can be formed with a stock reamer.

duced results for each die within close agreement. Therefore, the dimensions of the orifice as shown in figure 3 were adopted for all the test dies.

To determine whether the original taper of 3.58° had changed significantly during the tests, plaster casts were made of 14 dies which had shown high-wear losses. The angle to which each die had worn was determined from the average of eight measurements. The maximum angle calculated from the measurements was 3.85°, the minimum 3.43° and the average 3.66° or 0.08° greater than that of the angle to which the dies were originally made.

2. EXTRUSION APPARATUS

A screw-power beam and poise testing machine, capacity 20,000 pounds, was used for extruding the clay, the set-up for a test being shown in figure 4. The extrusion cylinder of the press was made of 6-inch wrought-iron pipe bored and fitted with a hard brass piston machined to a neat sliding fit. The piston was actuated by a detachable push rod and the upper, or exit end, was provided with a flange to which a removable head was bolted. A removable brass capsule was provided for holding the die and protecting ring, the capsule being threaded to fit into the center of the head.

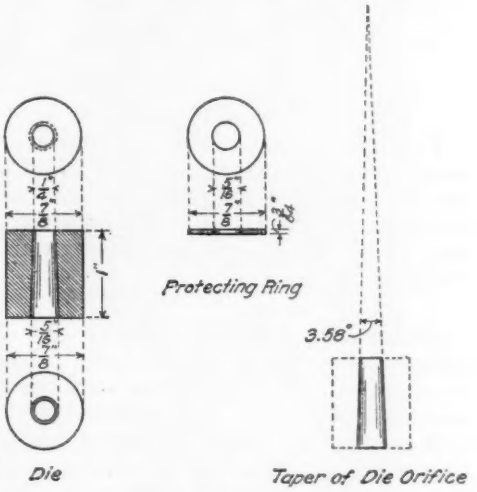

FIGURE 3.—*Dimensions of the die and protecting ring.*

The extrusion press was placed in the testing machine with the die exit upward. The push rod and piston remained stationary and the movable head of the testing machine carried the cylinder downward. The length of clay column extruded was determined by a measuring wheel and counter.

3. ABRADING MEDIUMS

Two abrasive mediums designated as clay no. 1 and clay no. 2 were used in making wear tests. Clays as prepared for the stiff mud process of manufacture generally lack uniformity in fineness of grain, plasticity, and amount and distribution of abrasive grains. They can, however, be made substantially uniform in particle distribution and working properties by repeated tempering and extrusion through a die.

(a) SELECTION OF CLAY NO. 1

A plastic Maryland clay was selected as the basis for preparing clay no. 1. The characteristics of the Maryland clay concerning fineness

of grain and plasticity were very similar to those of a ball clay. It had been used in a previous investigation [10] in which it had been repeatedly tempered and extruded from the die of a stiff mud auger brick machine and therefore it was thoroughly mixed and substantially constant in behavior.

In the preliminary tests this clay caused so little wear on the dies that it was necessary to produce larger and more conveniently measurable wear losses. Inasmuch as silica sand is the most predominant abrasive material of clays, a comparatively fine-grained glass sand was added to increase wear. Its sieve analysis is given in table 2.

TABLE 2.—*Sieve analysis of sand used in preparation of the abrasive clay no. 1*

U.S. standard sieve	Retained
Number	*Percent*
20	00.0
40	27.6
60	90.5
80	95.8
100	97.5

Preliminary tests indicated that a mixture of 60 parts clay and 40 sand, tempered with water to the stiff mud condition was satisfactory for the intended purpose. It was sufficiently plastic to flow well through the die, its abrasive intensity was approximately five times that of the Maryland clay alone, and it is hereinafter referred to as "clay no. 1."

(b) PREPARATION OF CLAY NO. 1

Sufficient quantities of the air-dry clay and sand were thoroughly mixed and stored in a closed bin. To obtain a satisfactory stiff mud consistency, batches of the mixture were tempered with different additions of water. It was found that the addition of approximately 14.8 percent by weight of the air dry clay-sand mixture produced the proper consistency. It developed, during the preliminary tests, that the extrusion pressure could not be maintained constant from day to day or from one test to another even though a definite amount of water had been added to the clay-sand mixture. The major cause [11] of this variation was apparently differences in evaporation with changes in relative humidity. A variation in extrusion pressure of as much as 8 percent was observed between days of very high and days of very low humidity. Inasmuch as extrusion pressure could not be maintained constant and since wear increased when extrusion pressure increases, it was necessary to determine the relation between extrusion pressure and wear so that the wear losses could be reduced to a comparable basis.

The earlier tests were made with a variation in water content from 14.7 to 15 percent which together with the uncontrollable factors, produced differences of 18 to 28 percent in extrusion pressure. This range of water content was selected to keep the limits of the tempered mass within the practical working range of stiff mud clay. However, it was later thought desirable to use a wider range of

[10] P. C. Grunwell, Studies of Machines for Extruding Clay Columns. Augers, Spacers, and Dies, B.S. Jour. Research, vol. 1 (RP 36), pp. 1023-1057, 1928.

[11] Enlargement of the die orifice and frictional resistance of the die material to flow of the abrasive also are influencing factors. This was especially pronounced in the case of the copper dies.

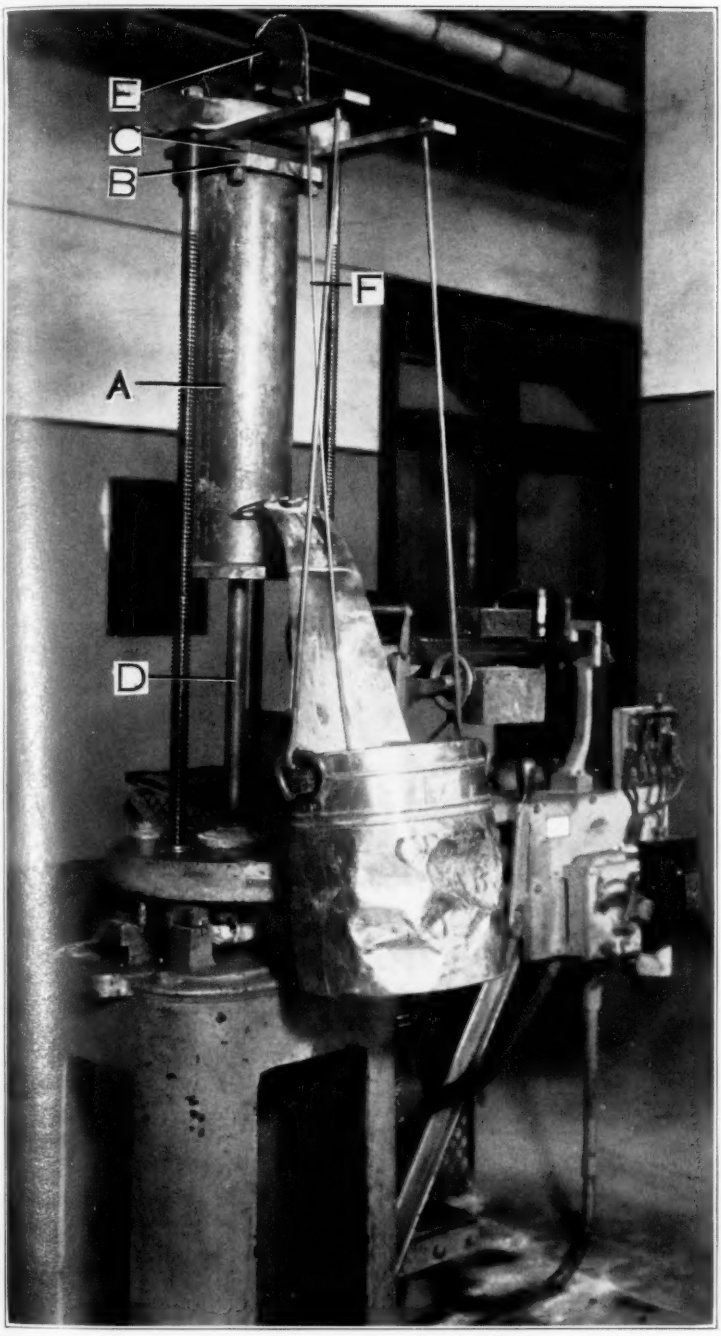

FIGURE 4.—*Complete assembly for wear tests showing the extrusion press in place in the testing machine.*

A, Cylinder; B, flange; C, head; D, push rod; E, measuring wheel; F, clay column

extrusion pressures to obtain a greater spread of the data, even though it would require that the clay be tempered to a consistency too stiff at one end of the range and too soft at the other for a commercial working stiff mud clay. Preliminary tests indicated that the addition of 14.36 to 15.05 percent water for tempering produced about the maximum range of workability. The difference of 0.69 percent water content together with the uncontrollable factors affecting pressure produced a variation in extrusion pressure of 33 to 50 percent.

(c) CLAY NO. 2

A porcelain body used as the abrasive to determine its abrasive intensity in comparison with that of clay no. 1 was received in the air dry condition from the manufacturer of the porcelain dies. It was substantially of the same composition as the mixture from which the dies had been made and it had been ground sufficiently fine to pass a no. 180 sieve.

In the preliminary tests to determine the proper water content for the desired range of stiff mud consistency, it was found that from 33 to 35.5 percent water by weight of the air dry material was required. The porcelain body in the plastic condition is hereinafter called clay no. 2.

(d) TEMPERING PROCESS

Clays nos. 1 and 2 were tempered by mixing the proper weights of the air dry material and of water required for each test. The tempering was done in a closed pug mill to lessen evaporation and 30 minutes was ample to insure thorough tempering and uniform consistency.

4. TEST PROCEDURE

(a) EXTRUSION

The tempered mass was removed from the pug mill in small portions at a time and thoroughly tamped into the extrusion cylinder. When the cylinder was full the top was leveled off and the head bolted in place. The die to be tested and its protecting ring were placed in the retaining capsule and the capsule inserted in the head. The cylinder was immediately placed in the testing machine and the extrusion made at a constant rate of piston displacement.

The time required to complete an extrusion was $32 \pm \frac{1}{6}$ minutes and the piston load readings were made at half-minute intervals during the total piston travel of 19 inches (48.26 cm), leaving a cake 1¼ inches (3.175 cm) thick between the piston and cylinder head. The average length of clay column extruded was 875 feet (266.7 m).

After the initial increase during the first 2 or 3 minutes, the load remained constant within about ±150 pounds (±68.04 kg) until about the 27th minute, when the close approach of the piston to the head caused the load to increase. A typical plot of the load against piston travel (also time) is shown in figure 5. The approximately horizontal part of the curve obviously corresponds to working conditions with constant feed and the average load over this part of the travel was considered as representing what would happen under such conditions. This average load expressed in kg/cm^2 of piston area will hereinafter be referred to as the "extrusion pressure" and denoted by p.

(b) AVERAGE DIAMETER AND AREA OF CLAY COLUMN

The average diameter of clay column and its area were calculated from the length of column and the constant volume extruded. The length of extruded column decreased 0.3 percent during three tests of the most wear-resistant dies and 40 percent approximately for three tests of the least wear-resistant dies.

(c) WEAR LOSS AND DEPTH OF WEAR

The die was weighed to one tenth of a mg before and after the test and the difference representing the wear was expressed in mm ^{3}.

The depths, or thicknesses, of the layers of material removed by wear from the nitrided-steel and the porcelain dies were determined indirectly. This method depends upon the assumption that the

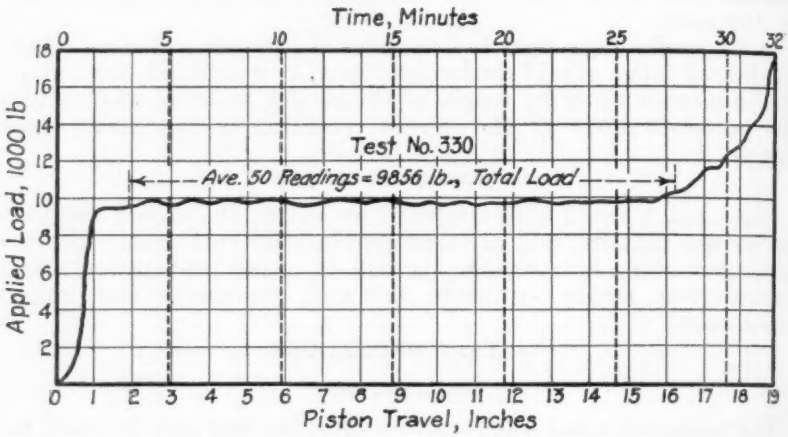

FIGURE 5.—*Relation between piston load and piston travel during a wear test.*

difference between the average diameter of the clay column of one test and that of another is equal to twice the thickness of the layer removed from the die by wear when the die has an angle of constant wear rate. This method of determining depth proved to be more sensitive and consistent than measurements by either a plug gage or an optical micrometer.

IV. RESULTS

1. WEAR COEFFICIENT

As the orifice of the die was enlarged by wear, the length and surface area of a given volume of the clay column decreased, hence the effective abrading area of the clay decreased. Obviously the wear of successive tests of a die, or tests of different dies, must be reduced to a common basis to be comparable.

Analysis of the data from more than 200 tests indicated that the wear for any one material was directly proportional to the surface area of the extruded clay column; therefore, the mm ^{3} wear loss per m ^{2} area of clay column was chosen as the common basis, or wear coefficient, and it is hereinafter designated as y.

2. RELATION OF WEAR COEFFICIENT, PRESSURE, WEAR RESISTANCE COEFFICIENT OR SERVICE VALUE, AND RELATIVE WEAR RATE

The wear coefficients and corresponding extrusion pressures were plotted logarithmically for each die material of substantially uniform wear rate.[12]

The plots for the different materials were all straight lines of very nearly the same slope. The relation between wear coefficient and extrusion pressure is:

$$\log y = m.\ \log.\ p - \log.\ K$$

or

$$y = \frac{p^m}{K}$$

in which y is the wear coefficient; p is extrusion pressure; K is wear resistance coefficient, also relative service value, and is constant for a material of uniform wear, and m is constant for all of the materials.

For this particular mode of testing and for the given units adopted for y and p, K is a specific constant for a die material of uniform wear resistance and represents its ability to withstand abrasion; that is, its relative service value. The reciprocal of K represents relative wear rate (v); (see p. 505 and fig. 2).

The service value may be considered as the length of time the die operates or the length of clay column extruded under constant working conditions which produces a definite volume wear loss.

3. RELATIVE WEAR RESISTANCE

The data were obtained on from 8 to 18 tests for each material. The extrusion pressure of 25 kg/cm^2 (355.6 lb/in.^{2}) lies close to the mean extrusion pressures for the different materials tested. The wear losses expressed as y were therefore calculated at $p = 25$ kg/cm^2 and are shown for comparison in column 3 of table 3. It is seen that the y values vary from 45.46 for the brass to 0.0869 for a chromium-cobalt-tungsten alloy.

The values of the exponent m determined experimentally are shown in column 4. The lowest m value is 1.511 for cast iron no. 8 and the highest 1.577 for stainless steel no. 15. The average for all tests of uniformly wearing dies is 1.548. No satisfactory m value was obtained for the cast electrolytic copper, which proved to be somewhat spongy and wore unevenly.

The comparative service values K (wear resistance coefficients, column 5, table 3) were calculated on the assumption that $m = 1.548$ for all the materials. The lowest service value is shown by the brass, and that of the copper is evidently lower than otherwise would be the case because of its spongy structure. There is no uniform gradation in service values from the lowest to the highest. The stainless steels and cast irons are all grouped within service values from 21.56 to 27.01. The chromium tool steel dies range in service value from 38.26 to 147.8, which may primarily be due to differences in their heat treatments. There is a difference of 404.8 in service value between chromium tool steel no. 21 and chromium-molybdenum steel

[12] Dies of nitrided steel and of porcelain showed unequal wear with depth.

no. 3 and also a wide margin between no. 3 and the chromium-cobalt-tungsten alloys nos. 11, 12, and 13. The type composition of no. 11 is different from that of nos. 12 and 13. The two latter, although of the same type composition, show a difference of 272 in service value. This difference for the most part may be due to the different methods by which they were cast.

TABLE 3.—*Wear coefficients y at 25 kg/cm² extrusion pressure, experimental values for constants m, relative service values K when m=1.548; and Vicker's hardness numbers*

No.	Material	Experimental		Calculated	Vicker's[1] numbers
		y	m	K	
10	Brass	45.46	1.529	3.22	170
9	Copper	[2] 22.98		6.35	41
14	Stainless steel	6.789	1.546	21.56	170
8	Cast iron	6.394	1.511	22.91	165
15	Stainless steel	6.021	1.577	24.38	210
5	Cast iron	5.560	1.558	26.32	157
6	do	5.557	1.538	26.32	164
7	do	5.483	1.543	26.72	174
16	Stainless steel	5.407	1.558	27.01	328
19	Cr-tool steel	3.832	1.555	38.26	188
20	do	3.533	1.565	41.57	188
23	do	3.202	1.563	45.63	360
22	do	2.531	1.563	57.82	531
17	Carbon steel	2.037	1.538	72.05	605
21	Cr-tool steel	0.9906	1.575	147.8	750
3	Cr-Mo steel	.2650	1.546	552.6	699
11	Cr-Co-Wo alloy	.1057	1.524	1,377	604
13	do	.1034	1.543	1,401	641
12	do	.0869	1.531	1,673	687
4	Nitrided steel K decreased from 115.1 for the first test to 70.8 for the ninth test.				
12	Porcelain K decreased from 107.7 for the first test to 66.3 for the twelfth test.				

[1] Each Vicker's number is the average of 12 determinations.
[2] Calculated on the average wear loss y, average extrusion pressure P, and average m (1.548).

4. SERVICE VALUES COMPARED WITH VICKER'S NUMBERS

The Vicker's numbers [13] are given in the last column of table 3. No correlation exists between hardness numbers and service values for unlike materials. For instance, the brass has a service value of 3.22 and a hardness number of 170, while stainless steel no. 14 has the same hardness number and a service value of 21.56. However, there is in general a direct relation between hardness numbers and service values for like materials. This is observed in the cast irons nos. 5, 6, and 7, the stainless steels nos. 14, 15, and 16, the different heat-treated chromium tool steels nos. 19 to 23, inclusive, and the three cobalt-chromium-tungsten alloys nos. 11, 12, and 13. Alloy no. 12 has the highest service value, namely 1,673, with a hardness number of 687, whereas the chromium tool steel no. 21 heated to 1,650 F and hardened in air blast shows the highest hardness number (750) with a service value of only 147.8.

5. VARIABLE WEAR WITH DEPTH

(a) NITRIDED STEEL

Nine wear determinations were made on each of two duplicate nitrided steel dies (no. 4, table 1 and fig. 6). Successive tests for each die showed variable wear, although the results of corresponding tests

[13] Vicker's numbers were determined by engineering mechanics section, Bureau of Standards.

for the two dies showed approximate agreement. The wear resistance coefficient K was, therefore, calculated for each test. These values were plotted against corresponding depths of wear in millimeters as shown in figure 6.

No photomicrograph was made of the dies, but the course of the curve of figure 6 indicates the existence of three different layerlike parts to a depth of about 0.105 mm (0.00413 in.). From a depth of 0.005 mm (0.0002 in.) to approximately 0.04 mm (0.00157 in.) the K value decreases from about 116 to 67. The second portion lies

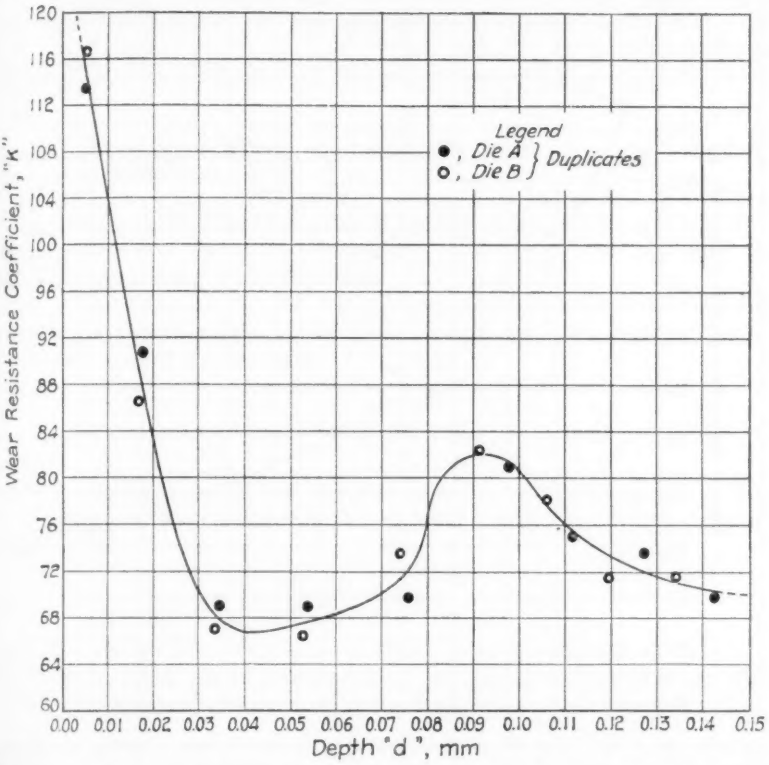

FIGURE 6.—*Relation between wear resistance coefficient and mm depth of abrasion for nitrided steel.*

between depths of near 0.04 to 0.075 mm (0.00157 to 0.00295 in.) in which the K value increases slightly. The third portion shows a sharp increase in K value to its maximum of 82 at a depth of approximately 0.093 mm (0.00366 in.) and beyond this depth the K value decreases.

At the end of the ninth test an average of 7,800 feet (2,377 m) of clay column had been produced for each die, equal in length to one from a brick machine which would yield approximately 38,400 side-cut face brick, or about a half-day's operation for an ordinary auger brick machine. This length of clay column had produced a wear depth of 0.14 mm (0.0055 in.), where the K value was approximately 70.78. Not all of the case had been removed, but the more wear-resistant part had disappeared and it is probable from the hardness numbers

at depths of 0.005 to 0.015 inch (0.127 to 0.381 mm) reported by Harder, Gow, and Willey [14] for a number of nitrided specimens that the K value would continue to decrease down to the depth of the untreated steel.

(b) PORCELAIN

The data obtained from 12 consecutive tests for each of the porcelain dies (no. 24, table 1 and fig. 7) showed an increasing rate of wear

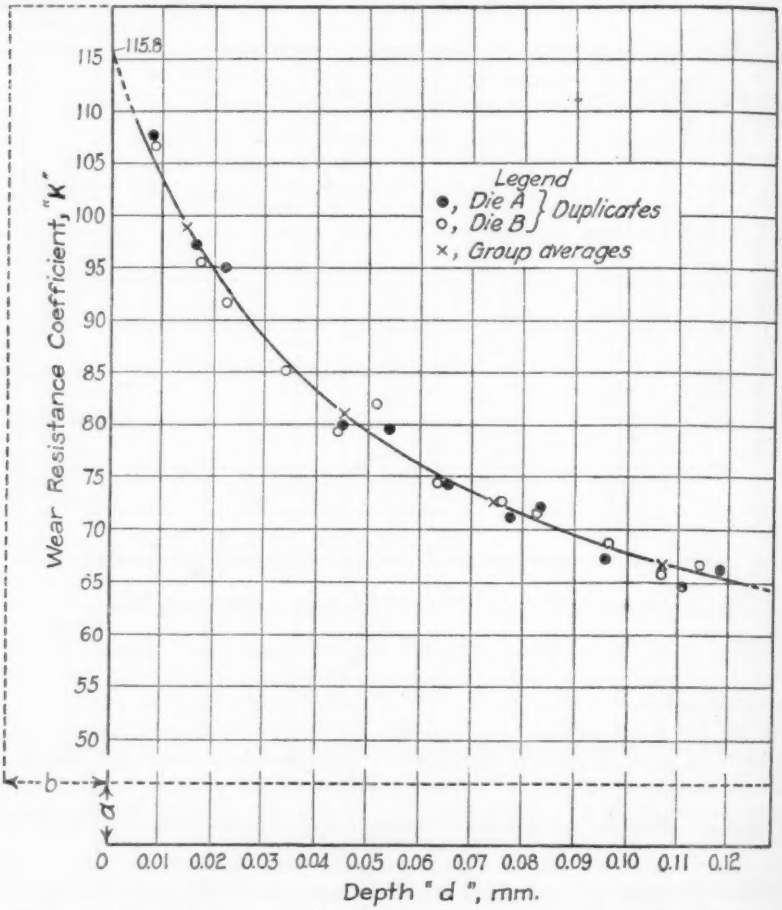

FIGURE 7.—*Relation between wear resistance coefficient and mm depth of abrasion for the porcelain.*

which appeared to approach a constant value, and corresponding tests of the dies showed reasonably close agreement. This increasing rate of wear was due to the so-called skin or hard outer portion of the porcelain which was evidently developed during the kiln treatment. The K value, calculated for each test, was plotted against depth in millimeters as shown in figure 7. Each of the 4 group averages represents the average of 3 consecutive duplicate tests.

[14] Trans. Am. Soc. Steel Treating, vol. 16, no. 5, p. 132, 1929.

The relation obtained between the K value and depth within the experimental limits is of the form:

$$(K-a)\ (d+b)=G$$

where K is wear resistance coefficient; d is depth, and a, b, and G are constants. Calculated on the values of the group averages, the values of the constants are approximately: $a=45.78$, $b=0.0462$, $G=3.235$.

The results obtained indicate that the K value decreases asymptotically with depth to some minimum value and that no break appears in the curve to indicate an abrupt change in the character of the hard outer portion of the porcelain. Theoretically, the minimum and maximum values of K for the porcelain are 45.78 and 115.8, respectively.

6. RELATIVE ABRADING INTENSITIES OF CLAYS NOS. 1 AND 2

Sixteen tests were made with clay no. 2 as the abrasive to obtain data for comparing its abrasive intensity with that of clay no. 1. These tests were made on chromium tool steel dies 21A and 21B previously tested for wear resistance to clay no. 1.

The data obtained for the wear losses (wear coefficient z) and the corresponding extrusion pressures p, when plotted logarithmically, showed the following relation:

$$z=\frac{p^{0.866}}{80.64}$$

while the equation obtained with clay no. 1 as the abrasive and the same dies gave the relation between wear coefficient y and extrusion pressure p as:

$$y=\frac{p^{1.575}}{160.5}$$

From these equations the expression $\frac{z}{y}=\frac{1.99}{p^{0.709}}$ is obtained from which the approximate relative abrasive intensities of the two abrasive mediums can be determined at any pressure within the limits covered by the tests.

In figure 8 the numerical y and z values are plotted against corresponding extrusion pressures which ranged from 17 to 29 kg/cm^2, (214.8 to 412.4 lb/in.^{2}). At the former pressure, $\frac{z}{y}=\frac{1}{3.75}$ and at the latter, $\frac{z}{y}=\frac{1}{5.47}$.

V. SUMMARY AND CONCLUSIONS

A study was made of dies of 20 metals and alloys and dies of porcelain to determine their relative resistances to wear by a plastic clay-sand mixture termed clay no. 1. The approximate angle of constant wear rate was determined for the specific dies used in the study. In addition, tests were made on one die material to determine the relative abrasive intensities of a plastic porcelain body (clay no. 2) and clay no. 1. A constant volume of the abrasive material in the stiff mud condition was extruded from the dies at a constant volume rate and their wear losses determined. Vicker's hardness numbers of the specimens were also determined.

Analysis of the data warrants presentation of the following results and conclusions:

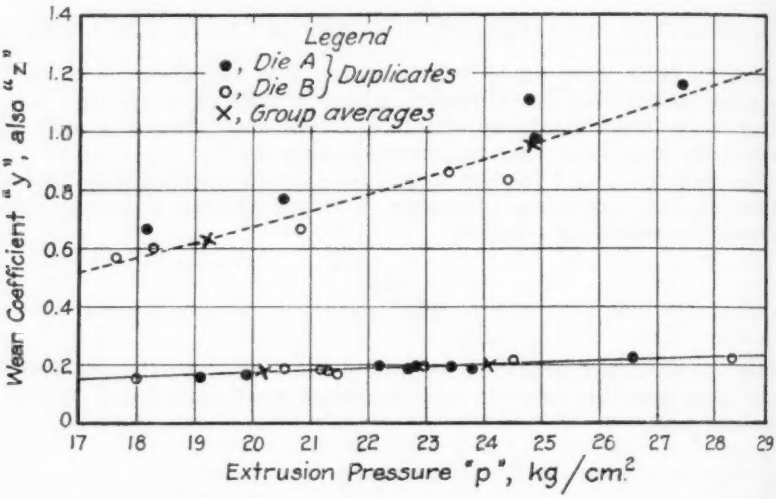

FIGURE 8.—*Relation between wear coefficient y and extrusion pressure p for tests with clay no. 1 (dotted line) and relation between wear coefficient z and extrusion pressure for tests with clay no. 2 (solid line).*

Tests made on chromium tool steel dies 21*A* and 21*B*.

1. The relative service values ranged from 3.22 for a brass to 1673 for a cobalt-chromium-tungsten alloy.

2. Tests of different dies of a chromium tool steel which had received five different heat treatments yielded service values from 38.26 for annealed dies to 147.8 for dies heated to 1,650 F and hardened in air blast.

3. Under constant working conditions, dies with cylindrical orifices wear toward a tapered orifice, with which orifice a wear rate constant within the limits of the tests was obtained. The relation between wear rate and time for a die in wearing from a cylindrical orifice to a taper of "constant wear rate" is of the character:

$$(a+u)\ (b-v)=R$$

in which v is wear rate; u is time equivalent; and a, b, and R are constants.

4. The relation between wear loss and extrusion pressure is of the character:

$$y=\frac{p^m}{K}$$

in which y is "wear coefficient"; p is extrusion pressure; m is constant for all materials; and K is "wear resistance coefficient", a specific constant for a die material of uniform wear resistance and represents its ability to withstand abrasion; that is, its "relative service value."

5. No correlation between Vicker's hardness numbers and service values was obtained for dies of unlike materials, but there is in general a direct relation for dies made of materials of the same character.

6. The wear resistance of nitrided steel dies decreased, increased, then decreased as layers at different depths of the case were removed. The relative wear resistence value for the first test was 116, while that for the ninth was 71 at a depth of 0.14 mm (0.00551 inch).

7. Within the experimental limits the wear resistance of porcelain dies decreases with depth asymptotically according to the equation:

$$(K-a)\ (d+b)=G$$

in which K is wear resistance coefficient; d is depth; and a, b, and G are constants. The numerical values obtained for the constants were: $a=45.78$, $b=0.0462$, and $G=3.235$.

8. Comparison of the relative abrasive intensities of a plastic porcelain body and a plastic clay-sand mixture on dies of one material was found to be $\frac{z}{y}=\frac{1.987}{p^{0.708}}$, in which z is wear coefficient when using the plastic porcelain body (clay no. 2) as the abrasive, y is wear coefficient when using the plastic clay-sand mixture (clay no. 1) as the abrasive, and p the extrusion pressure.

WASHINGTON, January 13, 1934.

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